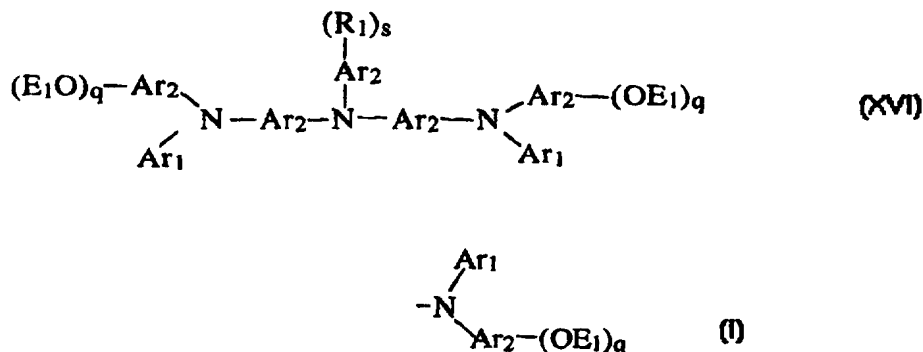




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(54) Title: CROSS-LINKABLE OR CHAIN EXTENDABLE POLYARYLPOLYAMINES AND FILMS THEREOF



(57) Abstract

A compound of formula (XVI), wherein R_1 is independently in each occurrence hydrogen or formula (i); Ar_1 independently in each occurrence is a C_{6-20} aromatic group or C_{3-20} heterocyclic group, optionally substituted with up to 5 C_{1-10} alkyl, alkoxy, thioalkoxy, aryloxy, or tertiary amine groups; Ar_2 is independently in each occurrence a C_{6-20} aromatic group, optionally substituted with up to 4 C_{1-10} alkyl, alkoxy, or thioalkoxy groups; E_1 is independently in each occurrence a C_{1-20} hydrocarbyl radical, or a group capable of chemically reacting in a chain-reaction or step-reaction polymerization process at a temperature of less than 300 °C at 1 atmosphere, with the identical group or other reactive groups attached to a separate monomer or polymer species, forming a covalent bond therebetween; and wherein the nitrogen atoms attached to the Ar_2 groups are located in positions which permit them to be in conjugation with any other nitrogen atom attached to the same Ar_2 group; q is an integer of from 1 to 4; and s is an integer from 1 to 4. Films of the compounds of the invention, as well as films of polymers of cross-linkable species of such compounds, are efficient in the transport of positive charges when exposed to relatively low voltage levels.

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CROSSLINKABLE OR CHAIN EXTENDABLE POLYARYLPOLYAMINES AND FILMS
THEREOF

5 This invention relates to crosslinkable or chain extendable polyarylpolyamines, methods for the preparation of such crosslinkable or chain extendable polyarylpolyamines and films thereof. The films of the polyarylpolyamines are useful as charge transport layers in light-emitting diodes.

10 Triarylamines, as evidenced by their low oxidation potentials, are easily oxidized to the corresponding radical cations. The cations are equally easily reduced to the neutral starting amines. This oxidation/reduction process is reversible and can be repeated many times. For this reason, triarylamines are widely used as charge transport materials, specifically for the transport of holes (positive charges).

15 Charge transport materials are essential to the efficient operation of electrophotographic devices (copying machines and printers) and electroluminescent devices such as light-emitting diodes. In both applications, the triarylamines are used in film form. For electrophotographic applications, a triaryamine and a polymeric binder are dissolved in a suitable solvent and the resulting solution used for coating, see U.S. Patents 5,352,554 and 5,352,834. Polycarbonates, polystyrene, poly(vinylcarbazole), poly(vinylbutyral) and 20 poly(methyl methacrylate) are some of the polymers used as binders. To obtain a film of useful charge transport properties, the loading of triaryamine in the final formulation must be as high as possible, preferably more than 30 percent of the total formulation with 50 percent by weight loading levels common. In low concentrations, the triaryamine will act to trap charge carriers instead of transporting them, D.M. Pai, J.F. Yanus, M. Stolka., J. Phys. Chem., Vol. 88, p. 4714 (1984). The triaryamine compound must be soluble in high 25 concentrations in the binder polymer after the film is formed and the solvent is removed. If the triaryamine compound separates out from the polymer binder or crystallizes into a fine dispersion of crystals in the polymer binder, the film can no longer serve its intended purpose.

30 Organic electroluminescent devices are typically constructed by sandwiching an organic film or a stack of organic films between an anode and a cathode such that when voltage is applied, holes and electrons are injected and transported into the device. The combination of holes and electrons within the organic layer leads to excitons which can undergo radiative decay to the ground state, emitting the excitation energy in the form of 35 light. For the light to be seen, it is necessary that one of the electrodes be transparent. Mixed metal oxides, particularly indium tin oxides (ITO), form smooth, conducting,

transparent films and are most commonly selected as the anode material. In practice, a sheet of ITO-coated glass is used as the substrate and onto the ITO side is deposited an organic film, and onto this film is deposited a second metal as the cathode. The cathode material is a metal of lower work function than ITO. Metals such as calcium, magnesium, indium and aluminum are used. A major improvement in device efficiency was achieved when a film of a triarylamine was deposited by conventional vapor-phase deposition between the emitting film and the anode, see C.W. Tang, S.A. Van Slyke, Appl. Phys. Lett., Vol. 51, p. 913 (1987), and U.S. Patent 4,539,507. One of the problems associated with devices of this type is the tendency of the organic films to crystallize due to the heat evolved during operation, see C. Adachi, T. Tsutsui, S. Saito, Appl. Phys. Lett., Vol. 56, p. 799 (1990). Contacts between organic layers and electrodes may be destroyed by crystallization, leading to device failure, see J. Kido, M. Kohda, Appl. Phys. Lett., Vol. 61, p. 761 (1992).

Copolymers consisting of aromatic amide and triarylamine groups have been claimed as hole-transporting layers in electroluminescent devices, see Japanese Patent 0531163-A. These copolymers are less desirable for use in electroluminescent devices as the concentration of the active triarylamine groups are depressed by the presence of the amide comonomer.

Organic electroluminescent devices are typically constructed by sandwiching an organic film or a stack of organic films between an anode and a cathode such that when voltage is applied, holes and electrons are injected and transported into the film layers. At least one of the layers is an "emitting" layer comprised of a compound or polymer. The combination of holes and electrons within this layer leads to excitons which can undergo radiative decay to the ground state, emitting the excitation energy in the form of light. For the light to be seen, it is necessary that one of the electrodes be transparent. Mixed metal oxides, particularly indium tin oxides (ITOs), form smooth, conducting, transparent films and are most commonly selected as the anode material. In practice, a sheet of ITO-coated glass is used as the substrate and onto the ITO side is deposited an emitting layer of an organic film, and onto this film is deposited a second metal as the cathode. The cathode material is a metal of lower work function than ITO. Metals such as calcium, magnesium, indium and aluminum are used.

U.S. Patent 4,539,507 describes depositing a film of a triarylamine by conventional vapor-phase deposition between the emitting film and the anode. U.S. Patent 5,256,945 describes a 4,4',4"-tris[N-(3-methylphenyl)-N-phenylamino]triphenyl-amine as a hole-transporting compound. Electroluminescent devices comprising vapor phase-deposited films of these aromatic amines have been shown to have good luminescence and durability. However, one of the problems associated with devices of this type is the tendency of the

amorphous organic films to crystallize due to the heat evolved during operation. Contacts between organic layers and electrodes may be destroyed by crystallization, thereby leading to device failure. Further, films prepared by vapor deposition methods may have limited usefulness in a device prepared by depositing a solution of an emitting polymer on a previously deposited layer of a hole-transport material. The vapor-deposited material may lack sufficient solvent resistance, or may be subjected to physical damage during the process of depositing the polymer thereon, depending on the particular process employed.

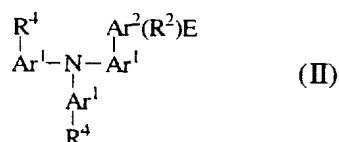
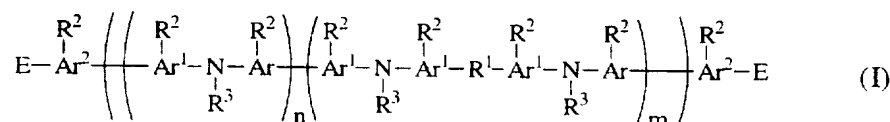
It is also known to prepare hole-transport layers by the application of a solution of thermoplastic polymers to a substrate. EP 0 372 979 describes hole-transporting thermoplastic polymers prepared from the reaction of aldehydes and aromatic amines. These polymers are freely soluble in common organic solvents, which may cause the layer thereof to degrade when a solvent-based composition containing the luminescent polymer is subsequently applied thereto.

EP 0 637 899 discloses an electroluminescent arrangement containing one or more organic layers, characterized by at least one of the layers being obtained by thermal or radiation-induced crosslinking and by the fact that it contains at least one charge-transporting compound per layer. Disclosed are known, relatively low molecular weight, charge-transporting compounds which carry anionically, cationically or radically polymerizable groups. Among the known charge-transporting compounds are tertiary aromatic amines, oxadiazoles, thiadiazoles, benzoxazoles, benzotriazoles, phthalocyanines, condensed aromatic systems such as perylenes, pyrenes or coronenes or polyene compounds. Radically polymerizable groups disclosed are vinyl carbonyl compounds such as acrylates, methacrylates or maleic acid derivatives. Cationically polymerizable groups are groups which react with protic acids or Lewis acids to form polymers and include vinyl ether and epoxide groups. Anionically polymerizable groups include cyanoacrylate, methacrylate or styrene. The compounds disclosed require large amounts of energy to result in excitation sufficient to cause light emission.

The invention relates to poly(tertiary di- or polyarylamines) further substituted with, on average, more than one aryl moiety which is further substituted with a moiety capable of chain extension or crosslinking. In another aspect, the invention relates to poly(tertiary di- or polyarylamines) further substituted with, on average, more than one aryl moiety which is further substituted with a moiety capable of chain extension or crosslinking, which are partially or completely crosslinked or chain extended. The invention further relates to films prepared from such chain extended or crosslinked poly(tertiary di- or polyarylamines). The invention further relates to electrophotographic devices and electroluminescent devices containing such films, such as polymeric light-emitting diodes.

The polymers of the invention form films which are efficient in the transport of positive charges when exposed to relatively low voltage levels. The films can be crosslinked to form solvent-resistant films. The processes disclosed herein provide efficient means of preparing the disclosed compounds.

In a preferred embodiment, the poly(tertiary di- or polyarylamines) of the invention correspond to Formula (I), (II), or (III).



Ar¹ and Ar² are independently in each occurrence a di- or multivalent C₆₋₁₈ aryl moiety or a di- or multivalent C₄₋₁₇ aryl moiety containing one or more heteroatoms of nitrogen, oxygen or sulfur. Preferably, Ar¹ and Ar² are independently in each occurrence derived from benzene, naphthalene, anthracene, phenanthracene, pyridine, thiophene, pyrrole, furan, diazine or oxazine. Even more preferably, Ar¹ and Ar² are derived from benzene. The aryl moieties may optionally be substituted. Preferred moieties substituted on the aryl moieties include alkyl and alkoxy moieties. More preferred moieties substituted on the aryl moieties include C₁₋₂₀ alkyl and C₁₋₂₀ alkoxy moieties. Even more preferred moieties substituted on the aryl moieties include C₁₋₁₀ alkyl and C₁₋₁₀ alkoxy moieties. Most preferred moieties substituted on the aryl moieties include C₁₋₄ alkyl and C₁₋₄ alkoxy moieties.

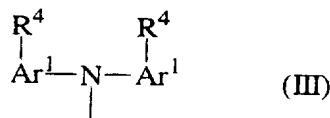
E is independently in each occurrence a hydroxy, glycidyl ether, acrylate ester, methacrylate ester, ethenyl, ethynyl, vinylbenzyloxy, maleimide, nadimide, trifluorovinyl ether, a cyclobutene bound to adjacent carbons on Ar², or a trialkylsiloxy. Even more preferably, E is a hydroxy, glycidyl ether, acrylate ester, methacrylate ester, ethenyl, ethynyl, maleimide or cyclobutene bound to adjacent carbons on Ar².

R¹ is independently in each occurrence a single bond; a sulfur; oxygen; C₁₋₂₀ divalent hydrocarbyl; a divalent silyl or polysilyl moiety bearing a C₁₋₁₀ hydrocarbyl moiety; a C₁₋₂₀ divalent hydrocarbyl further containing one or more of oxygen, sulfur, an arylamine, a carbonyl, a carbonyloxy, an amide, sulfinyl, sulfonyl, an aryl phosphinyl, or an aryl phosphine oxide; or a C₁₋₂₀ hydrocarbyl-substituted siloxy or polysiloxy. Preferably, R¹ is independently in each occurrence a single bond, a sulfur, oxygen or a C₁₋₂₀ divalent hydrocarbyl. Even more preferably, R¹ is independently in each occurrence a single bond, a sulfur, oxygen or a divalent benzene moiety.

R^2 is any substituent which does not interfere with the processing and the charge transport properties of the poly(tertiary di- or polyarylamine) and is preferably independently in each occurrence H, C_{1-20} hydrocarbyl, C_{1-20} hydrocarbyloxy, C_{1-20} hydrocarbyl thioether, C_{1-20} hydrocarbyl sulfonyl, C_{1-20} hydrocarbyl sulfinyl, or two adjacent R^2 bonded to two of Ar^1 which are bonded to the same nitrogen atom to form a direct bond between the two aromatic rings or are bound to a divalent sulfur or divalent oxygen. Preferably, R^2 is independently in each occurrence C_{1-20} hydrocarbyl or two adjacent R^2 bonded to two aromatic rings which are bonded to the same nitrogen atom to form a direct bond, or are bonded to a divalent sulfur or oxygen. Even more preferably, R^2 is independently in each occurrence C_{1-10} alkyl or two adjacent R^2 bonded to two aromatic rings which are bonded to the same nitrogen atom to form a direct bond, or are bonded to a divalent sulfur or oxygen.

R^3 is independently in each occurrence a C_{1-20} hydrocarbyl moiety or a moiety corresponding to the formula: $-Ar^1(R^2)-Ar^2-E$. Preferably, R^3 is independently in each occurrence a C_{1-20} alkyl, or C_{6-18} aryl moiety or a moiety corresponding to the formula: $-Ar^1(R^2)-Ar^2-E$. Even more preferably, R^3 is independently in each occurrence phenyl or a moiety corresponding to the formula: $-Ar^1(R^2)-Ar^2-E$.

R^4 is independently in each occurrence hydrogen, a C_{1-20} hydrocarbyl moiety, $-Ar^2(R^2)-E$ or a moiety corresponding to Formula (III):



with the proviso that each poly(tertiary di- or polyarylamine) contains, on average, two or more units which are $-Ar^2(R^2)-E$. Preferably, R^4 is independently in each occurrence hydrogen, a C_{1-10} alkyl moiety, $-Ar^2(R^2)-E$ or a moiety corresponding to Formula (III) with the proviso that each poly(tertiary di- or polyarylamine) contains, on average, two or more units which are $-Ar^2(R^2)-E$. Even more preferably, R^4 is independently in each occurrence hydrogen, a methyl, $-Ar^2(R^2)-E$ or a moiety corresponding to Formula (III) with the proviso that each poly(tertiary di- or polyarylamine) contains, on average, two or more units which are $-Ar^2(R^2)-E$.

m is a number of from 0 to 50. More preferably, m is a number of from 0 to 20. Most preferably, m is a number of from 0 to 5.

n is a number of from 1 to 50. More preferably, n is a number of from 1 to 20. Most preferably, n is a number of from 1 to 10.

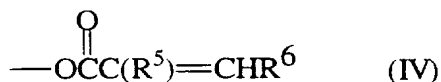
The poly(tertiary di- or polyarylamines) of the invention demonstrate strong photoluminescence in dilute solutions or in the solid state. When such materials are exposed to

light of a wavelength of 300 to 700 nanometers, the materials emit light of wavelengths in the region of 400 to 800 nanometers. More preferably, such materials absorb light of wavelengths of from 300 to 400 nanometers and emit light of wavelengths in the region of 400 to 650 nanometers. The poly(tertiary di- or polyarylamines) of the invention are readily soluble in common organic solvents. They are processable into thin films or coatings by conventional techniques. Upon curing, such films demonstrate resistance to common organic solvents and high heat resistance. The poly(tertiary di- or polyarylamines) of the invention are capable of crosslinking to form solvent-resistant, heat-resistant films at 100°C or more, more preferably at 150°C or more. Preferably, such crosslinking occurs at 350°C or less, more preferably 300°C or less and most preferably 250°C or less. The poly(tertiary di- or polyarylamines) of the invention preferably have oxidation potentials of +0.1 volt or greater, more preferably +0.4 volt or greater and preferably +1.0 volt or less, more preferably +0.7 volt or less.

The poly(tertiary di- or polyarylamines) of this invention preferably have a weight average molecular weight of 250 Daltons or greater, more preferably 500 Daltons or greater, even more preferably 1,000 Daltons or greater; preferably 1,000,000 Daltons or less, more preferably 500,000 Daltons or less and most preferably 100,000 Daltons or less. Molecular weights are determined according to gel permeation chromatography using polystyrene standards.

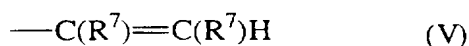
Preferably, the poly(tertiary di- or polyarylamines) having the sum of m and n of 5 or greater demonstrate a polydispersity (M_w/M_n) of 5 or less, more preferably 4 or less, even more preferably 3 or less, even more preferably 2.5 or less and most preferably 2.0 or less.

In a preferred embodiment, the acrylate and methacrylate ester reactive groups (E) on Ar^2 correspond to Formula (IV).



Preferably, R^5 is hydrogen or C_{1-4} alkyl and more preferably hydrogen or methyl. R^6 is preferably hydrogen, C_{1-20} hydrocarbyl or C_{1-20} hydrocarbyloxy. More preferably, R^6 is hydrogen or C_{1-20} hydrocarbyl. Even more preferably, R^6 is hydrogen, C_{1-10} alkyl or C_{6-10} aryl or alkyl-substituted aryl. Even more preferably, R^6 is hydrogen, C_{1-4} alkyl or phenyl. Most preferably, R^6 is hydrogen.

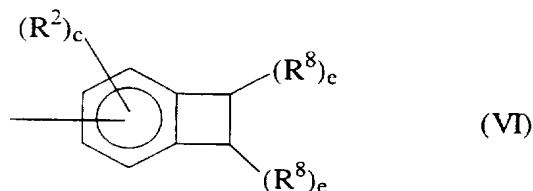
In a preferred embodiment, the ethenyl moiety (E) on Ar^2 corresponds to Formula (V).



Preferably, R^7 is independently in each occurrence hydrogen, C_{1-20} hydrocarbyl or C_{1-20} hydrocarbyloxy, more preferably hydrogen, C_{1-10} alkyl, C_{6-10} aryl or alkyl-substituted aryl or C_{1-20}

alkoxy. Even more preferably, R^7 is hydrogen, C_{1-4} alkyl, phenyl or C_{1-4} alkoxy. Most preferably, R^7 is hydrogen or methyl.

In one embodiment, E is a benzocyclobutene moiety which preferably corresponds to Formula (VI):

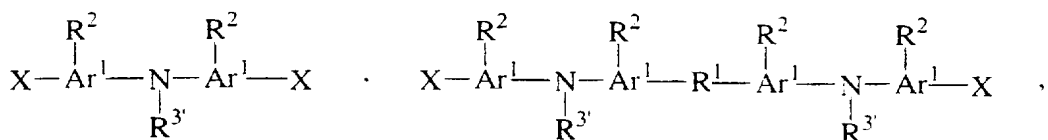


wherein:

R^2 is preferably C_{1-20} alkyl, C_{1-20} alkoxy, C_{1-20} alkylthio, C_{6-20} aryl, C_{6-20} aryloxy, C_{6-20} arylthio, C_{7-20} aralkoxy, C_{7-20} alkaryloxy, C_{7-20} alkarylthio, C_{7-20} aralkyl, C_{7-20} aralkoxy, C_{7-20} aralkylthio, C_{1-20} hydrocarbylsulfonyl or C_{1-20} hydrocarbylsulfinyl. R^2 is more preferably C_{1-20} alkyl. Most preferably, R^2 is C_{1-3} alkyl. R^8 is preferably C_{1-20} alkyl or C_{1-20} hydrocarbyloxy. c is an integer of 0 to 3. Preferably, c is from 0 to 1 and most preferably 0. e is an integer of from 0 to 2, preferably from 0 to 1 and most preferably 0.

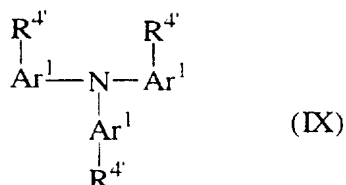
In one embodiment, the poly(tertiary di- or polyarylamines) are prepared by contacting one or more tertiary di- or polyarylamines having two halogen substituents with a haloaromatic compound having a reactive group capable of crosslinking or chain extension or a trialkylsiloxy moiety in the presence of a catalytic amount of a divalent nickel salt, at least a stoichiometric amount of zinc powder, a trihydrocarbylphosphine and a catalytic amount of a compound capable of accelerating the reaction in a polar solvent and an optional co-solvent comprising an aromatic hydrocarbon or ether. The nickel (zero valent) catalyst is prepared *in situ* by contacting a divalent nickel salt with a reducing agent in the presence of a material capable of acting as a ligand and optionally a material capable of accelerating the reactions.

The starting materials for this process are one or more tertiary di- or polyarylamines having 2 halogen substituents. The tertiary di- or polyarylamines preferably correspond to Formulas (VII), (VIII), and/or (IX):



(VII)

(VIII)

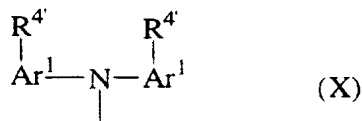


Ar¹ and R² are as defined previously.

X is independently in each occurrence halogen, more preferably chlorine or bromine, and most preferably bromine.

5 R³ is independently in each occurrence a C₁₋₂₀ hydrocarbyl moiety or Ar(R²)X. Preferably, R³ is independently in each occurrence a C₁₋₂₀ alkyl, C₆₋₁₈ aryl moiety or Ar(R²)X. More preferably, R³ is phenyl.

R⁴ is independently in each occurrence hydrogen, a C₁₋₂₀ hydrocarbyl moiety, X or a moiety corresponding to Formula (X):



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with the proviso that two units per molecule are X. Preferably, R⁴ is hydrogen, a C₁₋₁₀ alkyl moiety, X or a moiety corresponding to Formula (X) with the proviso that two units per molecule are X. More preferably, R⁴ is independently in each occurrence hydrogen, a methyl, X or a moiety corresponding to Formula (X) with the proviso that two units per molecule are X.

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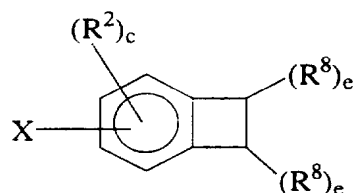
The tertiary di- or polyarylamines useful as starting materials in this invention preferably contain two halogen moieties. Such compounds are generally prepared by reacting tertiary di- or polyarylamines which do not contain a halogen with molecular halogen in a solvent such as a halohydrocarbon or a carboxylic acid. Alternatively, the tertiary di- or polyarylamines containing two halogen moieties may be prepared by contacting the tertiary di- or polyarylamines with bromosuccinimide in a polar solvent which dissolves the bromosuccinimide. This process is described by R.H. Mitchell, Y.H. Lai, and R.V. Williams in J. Org. Chem., Vol. 44, p. 4733 (1979). Examples of tertiary di- or polyarylamines which contain two halogen moieties include N,N-di-(4-bromophenyl)-p-toluidine, tri(4-

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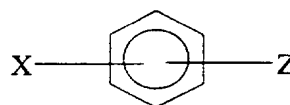
bromophenyl)amine, N,N'-di-(4-bromophenyl)-N,N'-di-(4-methylphenyl)benzidine, N,N'-di-(4-bromophenyl)-N,N'-di-(4-pentoxyphenyl)-benzidine, N,N'-di-(4-bromophenyl)-N,N'-di-(4-pentyloxyphenyl)-1,4-phenylenediamine, N,N'-di-(4-bromophenyl)-N,N'-di-(4-methoxyphenyl)-1,4-phenylenediamine and N,N-di-(4-bromophenyl)p-anisidine.

Examples of tertiary di- or polyarylamines useful in this invention include diphenyl-p-toluidine, N,N-diphenyl-p-anisidine, triphenylamine, N,N'-diphenyl-N,N'-di-(4-pentoxyphenyl)benzidine, N,N'-diphenyl-1,4-phenylenediamine, N,N'-diphenyl-N,N'-di-(4-methoxyphenyl)-1,4-phenylenediamine, N,N'-diphenyl, N,N'-di-(4-pentoxyphenyl)-1,4-phenylenediamine, N,N'-di-4(4'-hydroxybiphenyl)-N,N'-di-(4-pentoxyphenyl)benzidine, N,N'-di-4(4'-hydroxybiphenyl)-N,N'-di-(4-pentoxyphenyl)-1,4-phenylenediamine and N,N-di-(4-bromophenyl)p-anisidine.

Preferably, the haloaromatic compound having a reactive group capable of crosslinking or chain extension or a trialkylsiloxy moiety, corresponds to the formula: $E-Ar^2-X$ wherein Ar^2 , E and X are as previously defined. Preferably, the haloaromatic compound corresponds to Formula (XI) or Formula (XII).



(XI)



(XII)

Z is a trialkylsiloxy, glycidyl ether, acrylate ester, methacrylate ester, ethenyl, ethynyl, maleimide vinylbenzyloxy or a trifluorovinyl ether moiety. Preferably, Z is a trialkylsiloxy moiety, ethenyl, ethynyl, maleimide or trifluorovinyl ether moiety. More preferably, Z is a trialkylsiloxy moiety.

In one preferred embodiment, the haloaromatic compound is a halogen-substituted benzocyclobutene moiety according to Formula (XII).

Examples of haloaromatic compounds useful in this invention include bromostyrene, bromophenyl-trialkylsilyl ethers, bromobenzocyclobutene, N-(bromo-phenyl)maleimide, N-(bromophenyl)trifluorovinyl ether and N-(bromophenyl)nadimide.

The tertiary di- or polyarylamines having two halogen substituents and the haloaromatic compound may be contacted in a wide range of ratios, depending upon the desired degree of oligomerization or polymerization. Preferably, the mole ratio of tertiary di- or polyarylamines to haloaromatic compound is 0.5 or greater, preferably 1.0 or greater and more preferably 2 or greater. Preferably, the mole ratio is 50 or less, and more preferably 25

or less. Higher ratios facilitate the preparation of higher molecular weight oligomers and polymers.

In a preferred embodiment, the reaction of the tertiary di- or polyarylamines with the haloaromatic compound takes place according to the procedures of Colon et al. as described in Journal of Polymer Science, Part A, Polymer Chemistry Edition, Vol. 28, p. 367 (1990), and of Colon et al. as described in Journal of Organic Chemistry, Vol. 51, p. 2627 (1986).

The reactants are contacted in a polar solvent, preferably dimethylformamide, N,N-dimethylacetamide or N-methylpyrrolidinone. Up to 50 volume percent of a non-amide co-solvent can be used. Preferable co-solvents are aromatic hydrocarbons and ethers, for instance, tetrahydrofuran. The process is preferably conducted in the absence of oxygen and moisture, as the presence of oxygen is detrimental to the catalyst and the presence of a significant amount of water leads to premature termination of the process. More preferably, the reaction is performed under an inert atmosphere such as nitrogen or argon.

The catalyst is formed from a divalent nickel salt. The nickel salt may be any nickel salt which can be converted to the zero valent state under reaction conditions. Preferable nickel salts are the nickel halides, with nickel chloride and nickel bromide most preferred. The divalent nickel salt is present in an amount of 0.01 mole percent or greater, more preferably 0.1 mole percent or greater and most preferably 1.0 mole percent or greater based on the amount of haloaromatic compound and tertiary di- or polyaryl-amine present. The amount of divalent nickel salt present is preferably 30 mole percent or less, more preferably 15 mole percent or less based on the amount of haloaromatic compound and tertiary di- or polyarylamine present.

The reaction is performed in the presence of a material capable of reducing the divalent nickel ion to the zero valent state. Suitable material includes any metal which is more easily oxidized than nickel. Preferable metals include zinc, magnesium, calcium and lithium. The preferred reducing agent is zinc in the powder form. At least stoichiometric amounts of reducing agent based on haloaromatic compounds are required to maintain the nickel species in the zero valent state throughout the reaction. Preferably, 150 mole percent or greater, more preferably 200 mole percent or greater, and most preferably 250 mole percent or greater based on the haloaromatic compound and tertiary di- or polyarylamine is used. More preferably, the reducing agent is present in an amount of 500 mole percent or less, more preferably 400 mole percent or less and most preferably 300 mole percent or less based on the amount of haloaromatic compound and tertiary di- or polyarylamine.

The process is performed in the presence of a material capable of acting as a ligand. Preferred ligands include trihydrocarbylphosphines. More preferred ligands are triaryl or trialkylphosphines, with triphenylphosphines being the most preferred. The compound

capable of acting as a ligand is present in an amount of from 10 mole percent or greater, more preferably 20 mole percent or greater based on the haloaromatic compound and tertiary di- or polyarylamine. The compound capable of acting as a ligand is preferably present in an amount of 100 mole percent or less, more preferably 50 mole percent or less and most preferably 40 mole percent or less based on the amount of haloaromatic compound and tertiary di- or polyarylamine.

The reaction is performed in the presence of a compound capable of accelerating the reaction. Such accelerator comprises 2,2'-bipyridine or an alkali metal halide. Preferred alkali metal halides useful as accelerators include sodium bromide, potassium bromide, sodium iodide and potassium iodide. The most preferred accelerator is 2,2'-bipyridine. The accelerator is used in a sufficient amount to accelerate the reaction. Preferably, the accelerating compound is used in an amount of 0.1 mole percent or greater, preferably 0.5 mole percent or greater and most preferably 1.0 mole percent or greater based on the haloaromatic compound and tertiary di- or polyarylamine. Preferably, the accelerating compound is present in an amount of 100 mole percent or less, more preferably 50 mole percent or less and most preferably 5 mole percent or less based on the amount of haloaromatic compound and tertiary di- or polyarylamine.

The reaction can be performed at any temperature at which the reaction proceeds at a reasonable rate, but below the temperature which would cause the reactive group (E) to react. Preferably, the reaction is performed at a temperature of 25°C or greater, more preferably 50°C or greater and most preferably 70°C or greater. Below 25°C, the rate of reaction is unacceptably low. Preferably, the reaction is performed at a temperature of 200°C or less, more preferably 150°C or less and most preferably 125°C or less. Temperatures substantially higher than 200°C can lead to degradation of the catalyst. The reaction time is dependent upon the reaction temperature, the amount of catalyst and the concentration of the reactants. Reaction times are preferably 1 hour or greater and more preferably 10 hours or greater. Reaction times are 100 hours or less, more preferably 72 hours or less and most preferably 48 hours or less. The amount of solvent used in this process can vary over a wide range. Generally, it is desired to use as little solvent as possible. Preferably, 10 liters of solvent per mole of tertiary di- or polyarylamines or less are used, more preferably 5 liters or less is used, and most preferably 2 liters or less is used. The lower limit on amount of solvent used is determined by practicality, that is, handleability of the solution and solubility of the reactants and products in the solvent. The resulting poly(tertiary di- or polyarylamines) are recovered according to conventional techniques; preferred techniques include filtration and precipitation using a nonsolvent.

In another embodiment, the poly(tertiary di- or polyarylamines) may be prepared by a process disclosed by Ioyda et al. in Bulletin of the Chemical Society of Japan, Vol. 63, p. 80 (1990). Such method is similar to the method described hereinbefore. In particular, the catalyst is a divalent nickel salt introduced as a nickel halide bis-triphenylphosphine complex.

5 The reaction may be performed in a variety of solvents including acetone, dimethylformamide, tetrahydrofuran and acetonitrile. The reaction is accelerated by the addition of 10 mole percent of an organo-soluble iodide such as tetraethylammonium iodide. Such a reaction is performed at a temperature of from 20°C to 100°C for 1 to 24 hours.

In another embodiment, the subject compounds of the invention may be prepared via

10 the processes disclosed by Yamamoto in Progress in Polymer Science, Vol. 17, p. 1153 (1992). In such process, tertiary di- or polyarylamines containing two halogen substituents and the appropriate amount of reactive haloaromatic compounds are contacted with at least a stoichiometric amount of nickel catalyst in the form of nickel (1,5-cyclooctadiene) complex and at least a stoichiometric amount of 1,5-cyclooctadiene as a ligand in an inert solvent,

15 such as tetrahydrofuran. The reaction is preferably conducted at 70°C or higher for two or more days.

In another embodiment, the subject compounds of the invention may be prepared by the process disclosed by Miyaura et al. in Synthetic Communication, Vol. 11, p. 513 (1981), and by Wallow et al. in American Chemical Society Polymer Preprint, Vol. 34 (1), p. 1009

20 (1993). In such process, the halogens on the haloaromatic compound or the tertiary di- or polyarylamine are converted to the corresponding lithio- or Grignard moieties. Such processes are well known in the art (see, for example, March, Advanced Organic Chemistry, 2d Ed., pp. 408-414 (McGraw-Hill, 1977)). The tertiary di- or polyarylamine or haloaromatic compound is reacted with a trialkyl borate to form the corresponding boronic acid as

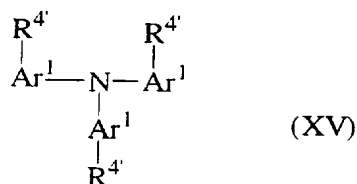
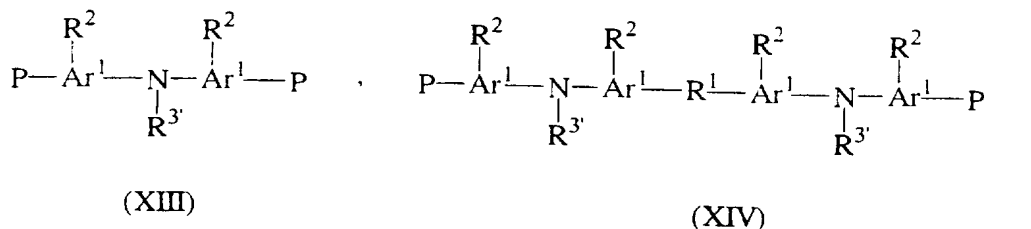
25 described, for example, by M. Rehalin et al. in Makromoleculaire Chemie, Vol. 191, pp. 1991-2003 (1990). The resulting boronic acid is reacted with the corresponding halogen-containing tertiary di- or polyarylamine or haloaromatic compound, respectively. In the embodiment where the poly(tertiary di- or polyarylamines) comprise more than one tertiary di- or polyarylamine and a single class of crosslinking or chain extension moiety, the aromatic

30 boronic acid substituted with the desired class of crosslinking or chain extension moiety is reacted with the appropriate halogen-substituted tertiary di- or polyarylamines. In the embodiment where the poly(tertiary di- or polyarylamines) comprise more than one class of crosslinking or chain extension moiety, the boronic acid derivative of the tertiary di- or polyarylamine is reacted with more than one haloaromatic compound having more than one

35 class of crosslinking or chain extension moieties. The boronic acid derivative is reacted with the appropriate halogenated tertiary di- or polyarylamines or haloaromatic compound in the

presence of a catalytic amount of tetrakis(triphenylphosphine)-palladium (0) and an aqueous base under conditions such that poly(tertiary di- or polyarylamines) are prepared.

The tertiary di- or polyarylamines useful in this process preferably correspond to Formulas XIII, XIV and XV:



The aromatic compound having a reactive group capable of crosslinking or chain extension, or a trialkylsiloxy moiety, preferably corresponds to Formula (XVI): E-Ar²-Q.

In Formulas (XIII), (XIV) and (XV):

E, Ar¹, Ar², R¹, R², R³, R³, R⁴, R⁴ and R⁴ are as previously defined;

P is a boronic acid, chloro or bromo moiety; and

Q is a boronic acid, chloro or bromo moiety, with the proviso that one of P or Q must be a boronic acid moiety and the other must be chloro or bromo.

The tertiary di- or polyarylamines and haloaromatic compound, in appropriate forms, may be contacted in a wide range of ratios, depending upon the desired degree of oligomerization or polymerization. Preferably, the mole ratio of tertiary di- or polyaryamine to haloaromatic compound is 0.5 or greater, preferably 1.0 or greater and more preferably 2.0 or greater. Preferably, the ratio is 50 or less, and more preferably 25 or less.

The tetrakis(triphenylphosphine)-palladium (0) may be generated *in situ* by the addition of a soluble palladium salt (for instance palladium acetate or palladium chloride) and at least four molar equivalents of triphenylphosphine.

The catalyst is present in a sufficient amount to promote the desired reaction and to facilitate a reasonable rate of reaction. Preferably, the catalyst is present in an amount of 0.01 mole percent or greater, more preferably 0.1 mole percent or greater and most preferably 1.0 mole percent or greater based on the amount of haloaromatic compound and tertiary di- or polyarylamines present. The tetrakis(triphenylphosphine)-palladium (0) is preferably present in an amount of 20 mole percent or less, more preferably 10 mole percent

or less and most preferably 5 mole percent or less based on the amount of haloaromatic compound and tertiary di- or polyarylamine present.

The reactants are contacted in a solvent which does not react with the reactants or deactivate the catalysts. Preferable solvents include aromatic hydrocarbons, lower alkanols, aliphatic ethers and N,N-dialkylamides; with toluene and ethanol being more preferred.

The process is preferably conducted in the absence of oxygen, as the presence of oxygen is detrimental to the catalyst. More preferably, the reaction is performed under an inert atmosphere such as nitrogen or argon.

The reaction can be performed at any temperature at which the reaction proceeds at a reasonable rate. Preferably, the reaction is performed at a temperature of 50°C or greater, more preferably 70°C or greater and most preferably 80°C or greater. Below 50°C, the rate of reaction is unacceptably low. Preferably, the reaction is performed at a temperature of 150°C or less, more preferably 130°C or less and most preferably 100°C or less.

Temperatures substantially higher than 150°C can lead to degradation of the catalyst. The reaction time is dependent upon the reaction temperature, the amount of catalyst and the concentration of the reactants. Reaction times are preferably 10 hours or greater and more preferably 20 hours or greater. Reaction times are 100 hours or less, more preferably 50 hours or less and most preferably 20 hours or less. The amount of solvent used in this process can vary over a wide range. Generally, it is desired to use as little solvent as possible. Preferably, 100 liters of solvent per mole of tertiary di-polyarylamine or less is used, more preferably 75 liters or less, and most preferably 50 liters or less. The lower limits on amount of solvent used is determined by practicality, that is, handleability of the solution and solubility of the reactants and products in the solvent. The resulting poly(tertiary di- or polyarylamines) are recovered according to conventional techniques; preferred techniques include filtration and precipitation using a nonsolvent.

In the embodiment wherein the reactive moieties on the poly(tertiary di- or polyarylamines) are trialkylsiloxy moieties, the trialkylsiloxy moieties may be converted to hydroxy moieties by contact with concentrated acid, such as hydrochloric acid, in an organic solvent. The hydroxy moieties may be converted to cyanate moieties by well-known cyanation reactions. See, for example, U.S. Patent 4,478,270; Martin, Organic Synthesis, Vol. 61, p. 35; and Handbook of Preparative Inorganic Chemistry, p. 1662 (1963), Academic Press, New York. In one preferred embodiment, the hydroxy-substituted poly(tertiary di- or polyarylamines) are contacted with cyanogen halide dissolved in a chlorinated hydrocarbon or a secondary or tertiary alcohol in the presence of a tertiary amine at a temperature of 0°C or less under conditions such that the hydroxy moieties are replaced with cyanate moieties. Preferably, the contacting occurs in the presence of a dilute base such as alkali or alkaline

metal hydroxides, alkali or alkaline metal carbonates, alkali or alkaline metal bicarbonates or tertiary amines. Preferred bases are the tertiary amines with the aliphatic tertiary amines being most preferred. This process is preferably run at a temperature of 0°C or lower with temperatures of -10°C or lower being most preferred. It is preferable to perform such

5 process under an inert gas atmosphere. The cyanated poly(tertiary di- or polyarylamines) may be recovered by washing the reaction solution with a dilute base to remove excess cyanogen chloride. The reaction solution is thereafter washed with water so as to remove any salt prepared from the hydrochloride by-product and base. The reaction solution is then

10 contacted with the dilute acid to neutralize any base which may be present. Thereafter, the reaction solution is contacted with water again so as to remove any other impurities and the cyanated poly(tertiary di- or polyarylamines) are recovered by drying the solution with the use of a desiccant.

In another embodiment, the hydroxy moieties of the hydroxy-substituted poly(tertiary di- or polyarylamines) may be converted to glycidyl ether moieties by processes well known

15 in the art. Such glycidyl ethers are preferably prepared by contacting the hydroxy-substituted poly(tertiary di- or polyarylamines) with epihalohydrin under conditions to form aryl moieties with chlorohydrin groups at their termini. The chlorohydrin groups are dehydrohalogenated to form an epoxy or glycidyl ring by contacting them with sodium hydroxide. Such process is described in Handbook of Epoxy Resins, McGraw-Hill, New York, New York USA (1967).

20 The poly(tertiary di- or polyarylamines) are useful in preparing coatings and films. Such coatings and films can be useful as charge transport layers in polymeric light-emitting diodes, in protective coatings for electronic devices and as fluorescent coatings. The thickness of the coating or film is dependent upon the ultimate use. Generally, such thickness can be from 0.01 to 200 microns. In that embodiment wherein the coating is used

25 as a fluorescent coating, the coating or film thickness is from 50 to 200 microns. In that embodiment where the coatings are used as electronic protective layers, the thickness of the coating can be from 5 to 20 microns. In that embodiment where the coatings are used in a polymeric light-emitting diode, the thickness of the layer formed is 0.05 to 2 microns. The compounds of the invention and their oligomers or polymers form good pinhole- and defect-

30 free films. Such films can be prepared by means well known in the art, including spin-coating, spray-coating, dip-coating and roller-coating. Such coatings are prepared by a process comprising applying a composition to a substrate and exposing the applied composition to conditions such that a film is formed. The conditions which form a film depend upon the application technique and the reactive end-groups of the aryl moiety. In a

35 preferred embodiment, the composition applied to the substrate comprises the poly(tertiary di- or polyarylamines) dissolved in a common organic solvent. Preferred solvents are

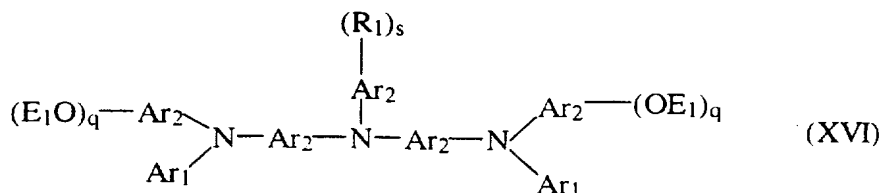
aliphatic hydrocarbons, chlorinated hydrocarbons, aromatic hydrocarbons, ketones, and ethers. It is preferable that such solvents have relatively low polarity. Preferably, the solution contains from 0.5 to 10 weight percent of the poly(tertiary di- or polyarylamine). For thin coatings, it is preferred that the composition contains from 0.5 to 5.0 percent by weight of the poly(tertiary di- or polyarylamine). This composition is then applied to the appropriate substrate by the desired method. The coating is then exposed to the necessary conditions to cure the film, if needed, to prepare a film having high solvent and heat resistance. The films are preferably substantially uniform in thickness and substantially free of pinholes.

Preferably, the films are cured when exposed to temperatures of 100°C or greater, more preferably 150°C or greater and most preferably 200°C or greater. Preferably, the films cure at a temperature of 300°C or less. Preferably, the films cure after exposure to the temperatures described previously for 10 minutes or greater. Preferably, the films cure after exposure to the temperatures described previously for 24 hours or less, more preferably 12 hours or less and most preferably 6 hours or less.

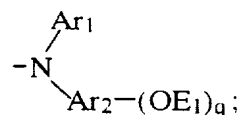
In the preparation of the films, the composition may further comprise a catalyst suitable to facilitate or initiate the curing of the films. Such catalysts are well known in the art; for instance, for materials having ethylenic unsaturation, a free radical catalyst may be used. For aryl moieties with glycidyl ethers as end-groups, ureas, and imidazoles may be used to improve or aid in curing. In the preparation of films from compounds of the invention with glycidyl ether aryl-terminal moieties, such materials may be reacted with commonly known curing agents which facilitate crosslinking. Among preferred curing agents are tetrahydrophthalic anhydride, nadic anhydride and maleic anhydride.

In another embodiment, the poly(tertiary di- or polyarylamines) may be partially cured. This is known as B-staging. In such an embodiment, the poly(tertiary di- or polyarylamines) thereof are exposed to conditions such that a portion of the reactive materials cure and a portion of the reactive materials do not cure. This is commonly used to improve the processability of such a resin and can facilitate the preparation of the films. Such B-staged material can thereafter be used to prepare coatings by the means disclosed hereinbefore. Preferably, 10 mole percent or greater of the reactive moieties are reacted. Preferably, 50 mole percent or less of the reactive moieties are reacted.

In another aspect, this invention is a compound of the formula:



wherein R₁ is independently in each occurrence hydrogen, or



Ar₁ independently in each occurrence is a C₆₋₂₀ aromatic group or C₃₋₂₀ heterocyclic group, optionally substituted with up to 5 C₁₋₁₀ alkyl, alkoxy, thioalkoxy, aryloxy, or tertiary amine

5 groups; Ar₂ is independently in each occurrence a C₆₋₂₀ aromatic group, optionally substituted with up to 4 C₁₋₁₀ alkyl, alkoxy, or thioalkoxy groups; E₁ is independently in each occurrence a C₁₋₂₀ hydrocarbyl radical, or a group capable of chemically reacting in a chain-reaction or step-reaction polymerization process, at a temperature of less than 300°C at 1 atmosphere, with the identical group or other reactive groups attached to a separate monomer or polymer
10 species, forming a covalent bond therebetween; and wherein the nitrogen atoms attached to the Ar₂ groups are located in positions which permit them to be in conjugation with any other nitrogen atom attached to the same Ar₂ group; q is an integer of from 1 to 4; and s is an integer from 1 to 4.

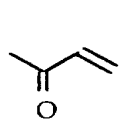
In another aspect, this invention is a polymer comprised of at least ten percent by
15 weight of units derived from a reactive species of the compound of Formula (XVI).

In another aspect, this invention is an electroluminescent device comprising a plurality of hole-transporting polymer films, at least one of which is the polymer described above, and a light-emitting polymer film, arranged between an anode material and a cathode material such that under an applied voltage, holes are injected from the anode material into the
20 hole-transporting polymer films and electrons are injected from the cathode material into the light-emitting polymer films when the device is forward biased resulting in light emission from the light-emitting layer and wherein the layers of hole-transporting polymers are arranged so that the layer closest to the anode has the lower oxidation potential, with the adjacent layers having progressively higher oxidation potentials.

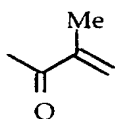
25 It has been discovered that the films of the compounds of Formula (XVI), as well as films of polymers of crosslinkable species of such compounds, are efficient in the transport of positive charges when exposed to relatively low voltage levels. Crosslinked films of crosslinkable species also possess good solvent resistance. Further, the processes disclosed herein provide an efficient means of preparing the disclosed compounds. Further,
30 the electroluminescent devices of the invention provide a relatively high light output at a relatively low voltage. These and other advantages of the invention will be apparent from the description which follows.

In Formula (XVI), Ar₁ preferably does not contain any optional substituents and is preferably phenyl, biphenyl, or naphthyl. Ar₂ also preferably does not contain any optional substituents and is preferably phenylene, naphthylene, or fluorene.

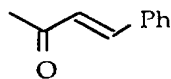
Examples of E₁ groups which are reactive include active hydrogen-containing groups, epoxide groups, and groups containing olefinic unsaturation (such as vinyl, acrylic, methacrylic). An active hydrogen-containing group is one that is reactive with the Zerewitinoff reagent according to the test described by Kohler in Journal of the American Chemical Society, Vol. 49, p. 3181 (1927). Examples of such groups include mercaptan, hydroxyl, primary and secondary amine, and acid groups. If E₁ is a reactive group and the compound is to be used in the preparation of an electroluminescent device, it should be relatively stable and non-reactive under the conditions it is applied to the ITO-coated glass. If the compound contains a reactive group, it preferably contains at least two of such groups so that the polymers of such compounds may be prepared. Examples of groups (E₁) which are reactive include -H,



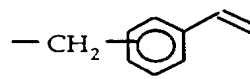
2A



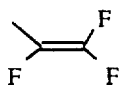
2B



2C



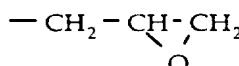
2D



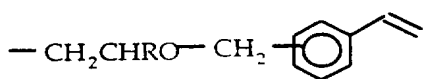
2E



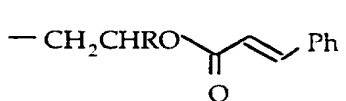
2F



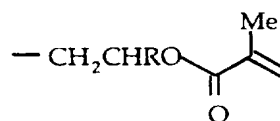
2G



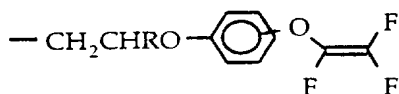
2H



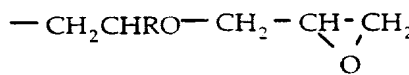
2J



2K



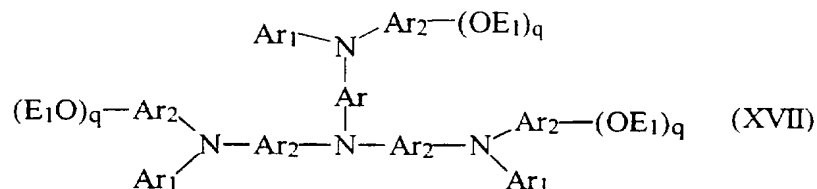
2M



2N

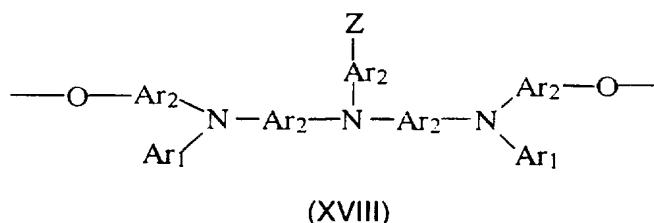
wherein R is independently in each occurrence selected from H, methyl, ethyl, butyl, or phenyl, but is preferably H. Preferably, E₁ is OH, methyl, benzyl, vinylbenzyl (2D), or acryloyl (2A).

In a preferred embodiment, Ar₁ is phenyl, Ar₂ is phenylene, q is 1, and E₁ is hydrogen, methyl, or benzyl. In another preferred embodiment, Ar₁ is phenyl, Ar₂ is phenylene, q is 1, and E₁ is vinylbenzyl or acryloyl. In the most preferred embodiment, Ar₁ is phenyl, Ar₂ is phenylene, q is 1, and E₁ is -CH₂CH₂-O₂CCH=CH₂. Further, any additional substituents for the Ar₂ groups bonded to two nitrogen atoms should be selected so that they do not interfere with its resonance. Preferably, R₁ contains a tertiary amine group as shown above, in which case the compound of the invention has the formula (when s=1):



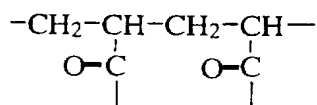
The compounds of the invention wherein E₁ is a non-reactive group (a C₁₋₁₀ hydrocarbyl radical) may be deposited onto a substrate as smooth, pin-hole free films by conventional vapor deposition techniques or by solution coating processes. Films of the aromatic amines wherein at least one E₁ is a reactive group may be prepared by solution-coating processes such as spin-coating, roller-coating, dip-coating, and spray-coating. These films are amorphous as evidenced by the absence of birefringence when examined under cross-polarized light and are also resistant to crystallization even at elevated temperatures (above 60°C).

The polymers of the invention contain at least two groups of the following formula:



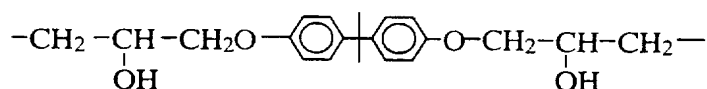
wherein Z is hydrogen, a C₁₋₁₀ hydrocarbyl, alkoxy, thioalkoxy, aryloxy or, if R₁ in the compound of Formula (XVI) contained a reactive group, a group of the formula: -N(Ar₁)Ar₂-O-, as well as residues of the unsaturated or reactive groups of the compound in Formula (XVI) and any groups derived from any crosslinkers and comonomers utilized in the preparation of the polymer. If, for example, the crosslinkable group is acryloyl, which will

react with other acryloyl groups, the group which links the groups shown above will have the formula:



(XIX)

5 In another example, if the reactive group is -OH and the diepoxide of bisphenol A is used as the crosslinking compound, the group which links the groups shown above will have the following formula:



(XX)

Such groups are present in the polymer in an amount, based on the weight of the polymer, of at least 10 percent, more preferably at least 20 percent; but preferably no greater than 75 percent, more preferably no greater than 50 percent. The polymers of the invention may be (a) chain-reaction homopolymers of compounds of Formula (XVI) containing unsaturated groups or copolymers of such compounds with other compounds containing unsaturated groups; or (b) step-reaction polymers of compounds of Formula (XVI) containing other reactive species and other compounds containing at least two groups per molecule which will react with such reactive species (hereafter referred to as "crosslinkers").

If the compound of Formula (XVI) contains unsaturated groups, the chain-reaction polymerization thereof may be carried out by heating or photoinitiation processes. For example, when E contains an acrylate or methacrylate moiety, crosslinking of the compounds can be effected by either heat or light. If the polymer of the invention is prepared by a step-reaction polymerization process, such process may be carried out under any reaction conditions suitable for the reaction of compounds containing the particular reactive species. If, for example, the reactive groups of the compounds of Formula (XVI) are epoxide groups, the polymer of the invention may be prepared by reacting such compounds with crosslinkers containing hydroxyl groups, such as bisphenol A or compounds containing amine groups such as methylene dianiline. In another embodiment of the invention, phenol derivatives of the compounds of the invention (Formula (XVI), wherein E₁ is H), may be crosslinked using a diepoxide such as, for example, a diepoxide of bisphenol A as a crosslinker.

30 The temperature for the thermal polymerization of compounds containing unsaturated groups is preferably selected so that a substantial percentage of the reactive groups may be converted over a period of 0.1 hour to 24 hours, but is dependent on the chemical nature of the reactive groups as taught by Hergenrother in "Reactive Oligomers", ACS Symposium

Series 282, American Chemical Society, Washington D.C., p. 1 (1985); and Percec and Auman [ibid, at p. 91]. Reactions involving trifluorovinyl ether groups are taught by Babb and coworkers in ACS Polymer Preprints, Vol. 34, No. 1, p. 413 (1993).

In another embodiment, the preparation of polymers from compounds containing acrylate or styrenic groups (Formula (XVI), wherein E₁ contains a terminal group of the Formulas 2A, 2D, 2F, or 2H) may be accelerated by the presence of 0.1 to 2 percent of a free radical initiator, for example, benzoyl peroxide, t-butyl perbenzoate, t-butyl peroctoate. Preferably, the polymerization is carried out at a temperature of at least 100°C and no greater than 300°C, more preferably no greater than 250°C, and most preferably no greater than 200°C. Preferably, the polymerization reaction is substantially complete in no more than 24 hours, more preferably no more than 12 hours, and most preferably in no more than 6 hours.

For radiation curing of methacrylates and acrylates (Formula (XVI), wherein E₁ contains a terminal group of the Formula 2A, 2B, 2F, or 2J) a combination of initiator and activator compounds may be required to cause crosslinking. Since the polymers of the invention may strongly absorb light from 300 nm to 375 nm, photoinitiators that are capable of absorbing light of wavelength longer than 375 nm are preferred. Thioxanthenes, particularly alkylated thioxanthenes which are suitable for the purpose, are described by M. J. Davis et al. in J. Oil Col. Chem. Assoc., Vol. 61, p. 256 (1978). It is preferred that thioxanthenes be used in conjunction with a photoactivator. Suitable photoinitiators are tertiary amines, such as dimethylaniline and ethyl 4-dimethylamino-benzoate.

Alternatively, 1,2-diketones may be used as a photoinitiator in conjunction with an amine photoactivator as taught by B. Martin in U.S. Patent 4,525,256.

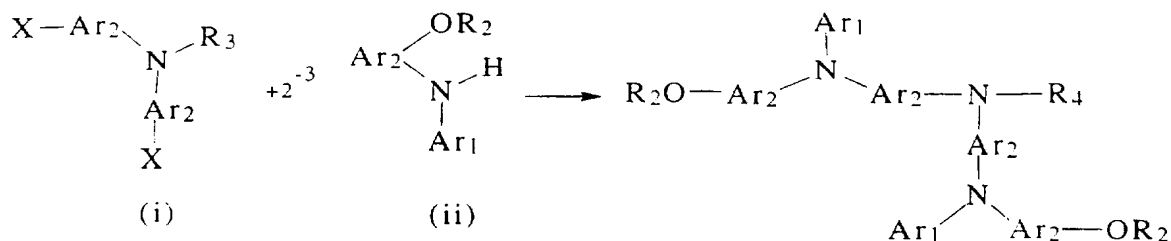
Preferably, the amount of photoinitiator is in the range of 0.1 to 5 phr (parts per hundred parts resin, based on the combined weight of the monomeric and polymeric species); the most preferred amount is in the range of 0.1 to 2 phr. The preferred amount of photoactivator is in the range of 0.3 to 10 phr; the most preferred amount is in the range of 0.5 to 3 phr.

Comonomers and crosslinkers may be selected to modify the film-forming behavior of the polymers. For example, a triacrylate compound of the invention may be blended with a monoacrylate or a diacrylate such as, for example, diethylene glycol diacrylate, and the resulting blend formed into films and then polymerized thermally or photochemically. The comonomers, acting as reactive diluent, need not be aromatic amines so long as the amount incorporated is not large enough to substantially interfere with the hole-transporting property of the film. The preferred amount of reactive diluent is no more than 25 weight percent of the total formulation, more preferably no more than 10 weight percent.

The preferred radiant energy level for polymerization is one that can lead to substantial crosslinking no more than 2 hours, more preferably no more than 1 hour, and most preferably no more than 30 minutes.

If so desired, the OE_1 group of the compound may be converted to a different OE_1 group in order to affect the reactivity of the compound of Formula (XVI) or the type of radiation which may be used to effect the polymerization thereof. For instance, the phenol derivative may be partially reacted with vinylbenzyl chloride and then reacted with acryloyl chloride to give a reactive aromatic amine containing vinylbenzyl ether and acrylate moieties. Alternatively, the phenol derivative may be converted to the corresponding epoxide (by reaction with epichlorohydrin) which may be polymerized using a variety of comonomers and initiators.

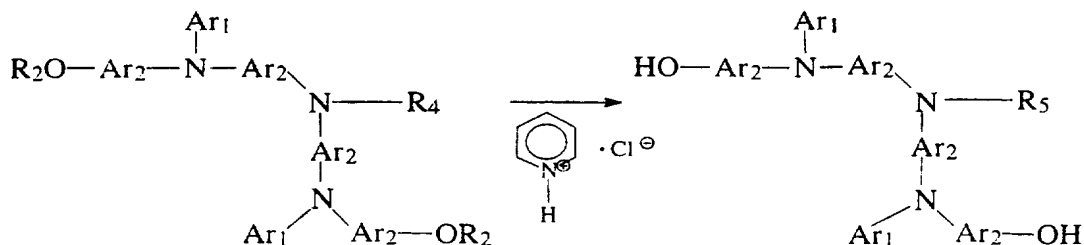
The compounds of the invention may be prepared by several techniques illustrated by Equations (1) and (2). Equation (1) illustrates the preparation of a compound having terminal groups of the formula $(-OR_2)$, wherein R_2 is a C_{1-10} alkyl group, from which compounds of the invention containing terminal phenolic groups may be derived. Equation (2) illustrates the preparation of the corresponding phenolic compound, from which the other compounds of the invention may be derived. Examples of starting materials for Equation (1) are (i) di- and tri-(4-halophenyl)amines (wherein the halogen is Br or I), which are reacted with (ii) a diarylamine having at least one substituent of the formula $(-OR_2)$, which are present in the reaction mixture in amounts sufficient to provide a molar ratio of (ii):(i) of greater than 2:1. The displacement of the halogen groups by the diarylamine may be carried out under any suitable reaction conditions for carrying out (a) an Ullman reaction or (b) a palladium-catalyzed displacement reaction as illustrated by Guram, Rennels and Buchwald in Angewandte Chemie International Edition in English, Vol. 34, p. 1348 (1995). Examples of processes for carrying out an Ullman reaction are described by R. Walker in Journal of American Chemical Society, Vol. 77, p. 5999 (1955), and by Gauthier & Frechet in Synthesis, p. 383 (1987). The Ullman reaction requires a di- or tri-(4-iodophenyl)amine as one of the starting materials while the corresponding bromo analog may be used in the palladium-catalyzed process. For the diarylamine reactant, it is preferred that R_1 be a lower alkyl group or a benzyl group and R_2 be methyl. The desired reaction product may be isolated by conventional techniques and purified by column chromatography on silica gel and recrystallization.



Equation (1)

In Equation (1), X is a halogen and R₃ is Ar, or Ar₂-X; R₄ is Ar, or -Ar₂-N(Ar₁)-Ar₂-OR₂.

Equation (2) illustrates conversion of ether groups of a di- or tris-ether compound to the corresponding phenolic compound. As shown below, the R₂ groups are replaced by hydrogens. This is accomplished by heating the tris-ether with a large excess of pyridine hydrochloride at 180°C or above, for a length of time sufficient to effect the desired displacement. It is preferred to employ at least 200 weight percent of pyridine hydrochloride relative to the tris-ether, with at least 300 weight percent being more preferred, and at least 400 weight percent being most preferred.



Equation (2)

In the above equation, R₅ is Ar, or -Ar₂-N(Ar₁)-(Ar₂-OH). Preferably, the reaction is carried out at a temperature of at least 180°; but is preferably no greater than 250°C, more preferably no greater than 225°C. The preferred reaction time is less than 10 hours, with less than 6 hours being more preferred.

Conversions of the di- or tris-phenol to the corresponding polymerizable esters or ethers may be accomplished through well-known processes for the preparation of esters and ethers from hydroxyl-containing compounds. Thus, the esters (acrylate, methacrylate and cinnamate) may be obtained by reacting the phenol derivative with the appropriate acid chlorides in the presence of a base. The tri-vinylbenzyl ether is obtained by reacting the trisphenol with vinylbenzyl chloride in the presence of a base, and the tri-epoxide is obtained by treating the trisphenol with epichlorohydrin in the presence of a base. Similarly, trifluorovinyl ether derivatives can be prepared by reacting the trisphenol with 1,2-dibromo-

tetrafluoroethane in the presence of a base, followed by dehalogenation (see Babb et. al. cited above). In the instances in which E₁ contains an oxyethylene moiety, the di- or tris-phenol is first reacted with either 2-bromoethanol or 2-chloroethanol to yield the corresponding tri(2-hydroxyethyl) ether, which is then converted to the corresponding
5 reactive species by, for example, reaction with an appropriate acid halide, as outlined above.

In another aspect, this invention is an electroluminescent device comprising a plurality of hole-transporting polymer films, at least one of which is the polymer of the invention, and a light-emitting polymer film, arranged between an anode material and a cathode material such that under an applied voltage, holes are injected from the anode material into the hole-
10 transporting polymer films and electrons are injected from the cathode material into the light-emitting polymer films when the device is forward biased resulting in light emission from the light-emitting layer and wherein the layers of hole-transporting polymers are arranged so that the layer closest to the anode has the lower oxidation potential, with the adjacent layers having progressively higher oxidation potentials.

The term "hole-transporting polymer film" as used herein refers to a layer of a film of a polymer which when disposed between two electrodes to which a field is applied and holes are injected from the anode, permits adequate transport of holes to the cathode. Hole-transporting polymers typically are comprised of triarylamine moieties. The term "light-emitting polymer film" as used herein refers to a layer of a film of a polymer whose excited
20 states can relax to the ground state by emitting photons, preferably corresponding to wavelengths in the visible range. Light-emitting polymers typically are comprised of π -conjugated segments. The term "anode material" as used herein refers to a semi-transparent, or transparent, conducting film with a work function between 4.5 electron volts (eV) and 5.5 eV. Examples are oxides and mixed oxides of indium and tin, and gold. The
25 term "cathode material" as used herein refers to a conducting film with a work function between 2.5 eV and 4.5 eV. Examples are lithium, calcium, magnesium, indium, silver, aluminum, or blends and alloys of the above.

To construct an electroluminescent device, one would first apply the compound of the invention onto an ITO glass. If a solution of the compound is utilized, the solvent is then
30 allowed to evaporate. If the compound contains reactive groups, polymers thereof may then be prepared by subjecting the compound to heat or light or by permitting the reactive groups to react with an appropriate crosslinker. A solution of the emitting polymer may then be applied on top of the layer created thereby; finally, a layer of a suitable metal film is deposited as the cathode. Preferably, one or more intermediate layers of a different hole transport
35 material is deposited between the layer containing the compound or polymer of the invention and the layer of light-emitting polymer. In such case, the intermediate layer preferably has a

reversible oxidation potential which is between the reversible oxidation potential values of the two layers between which the intermediate layer is sandwiched. In an alternative configuration, the layer containing the compound or polymer of the invention is itself sandwiched between two layers, one of which has a higher reversible oxidation potential, and the opposite layer having a lower one. By these methods, a hole-transport layer which is a composite of two or more hole-transport materials may be prepared, with the material closest to the light-emitting layer having an oxidation potential similar to the light-emitting material, and the layer adjacent to the metal anode having the lowest reversible oxidation potential. By this method, electroluminescent devices having relatively high light output per unit voltage may be prepared.

The following examples are included for illustrative purposes only and do not limit the scope of the claims. Unless otherwise stated, all parts and percentages are by weight.

Example 1

A. Preparation of N,N-di(4-bromophenyl)-p-toluidine

A solution of N-bromosuccinimide (138.23 g, 0.78 mol) in 300 mL of dimethylformamide (DMF) was slowly added with stirring to a solution of N,N'-diphenyl-p-toluidine (99.7 g, 0.38 mol) in 300 mL of dimethylformamide (DMF). The rate of addition was such that the reaction temperature was kept below 50°C. The reaction was stirred for an additional 15 minutes after the addition was complete. The reaction mixture was slowly added to water (300 mL) to precipitate the product. The crude product was recrystallized from ethanol to afford 153.4 g (85 percent) of slightly yellow crystals after drying overnight in a vacuum oven at 60°C.

B. Preparation of crosslinkable oligomer from N,N'-di(4-bromophenyl)-p-toluidine and bromobenzocyclobutene

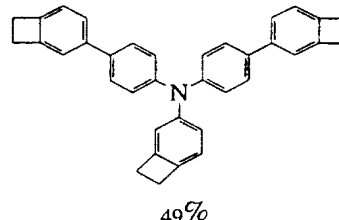
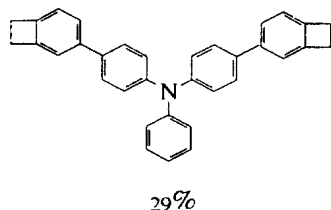
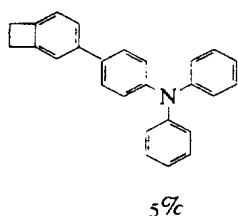
To a dry reactor equipped with a mechanical stirrer, nitrogen/vacuum inlet, and a rubber septum was added triphenylphosphine (3.9 g, 15 mmol), zinc powder (5.9 g, 90 mmol) and nickel chloride-2,2'-bipyridine complex (NiCl₂-Bipy) (0.26 g, 0.9 mmol). The reactor was evacuated to 0.2 mm Hg and was then purged with nitrogen. This cycle of evacuation and purging was repeated 7 times. To the reactor was added a solution of N,N-di(4-bromophenyl)-p-toluidine (12.51 g, 30 mmol) and bromobenzo-cyclobutene (BrBCB) (2.2 g, 12 mmol) in anhydrous N,N'-dimethylacetamide (DMAc) (45 mL). The reaction mixture was stirred at 80°C for 16 hours and then was added to dichloromethane (500 mL). The solution was filtered through a bed of filtering aid to remove the unreacted zinc and the filtrate concentrated on a roto-evaporator under reduced pressure. The concentrate was added to methanol to give a yellow precipitate. The yellow powder was collected and washed with ethanol (2 x 150 mL). The dried product was 9.12 g of a yellow powder containing a trace of

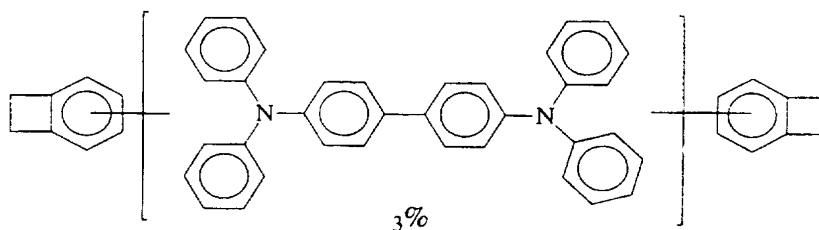
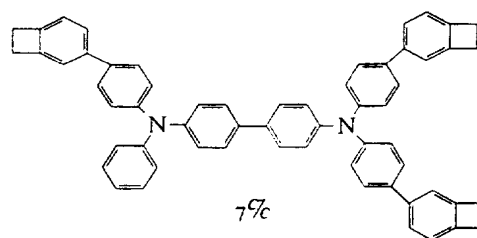
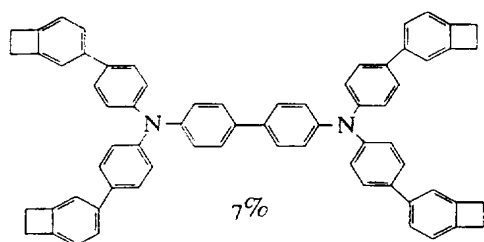
triphenylphosphine. It was refluxed in hexane (300 mL) for 30 minutes, collected in a Buchner funnel and washed with hot hexane (3 x 150 mL). After drying in a vacuum oven at 40°C for 4 hours, a pale yellow powder was obtained (8.05 g, 88 percent).

Proton NMR integration of the methylene protons of benzocyclobutene (BCB) versus the methyl protons was performed to determine the ratio of triarylamine unit to BCB, and the results are shown in Table I. Differential scanning calorimetry (DSC) analysis at 10°C/minute was performed on the polymer. UV absorption and photoluminescence spectra of a chloroform solution of the product were taken. A thin film spin-coated on a quartz plate from a 0.5 weight percent chloroform solution was heated at 2.5°C/minute to 250°C then held at 250°C for 1 hour. UV absorption and photoluminescence spectra of the film were taken. UV absorption of the cured film showed a slight shift of the peak maximum to 354 nm. Photoluminescence spectrum of the cured film showed an intense, broad emission peak at 490 nm and a minor peak at 420 nm. Cyclic voltammetry on the oligomer in solution and a film cured onto a carbon electrode was performed to determine reversible oxidation potentials. These data were compiled in Table I and demonstrated that crosslinking had no effect on the redox process and that the polymeric films were suitable for charge transport.

Example 2 - Coupling of bromobenzocyclobutene to tri(4-bromophenyl)amine

A tetrahydrofuran (THF) solution of BCB Grignard was prepared from 12.08 g (66 mmol) of BrBCB, 1.46 g (60 mmol) of magnesium turnings, and 20 mL of THF. To this solution was then added 0.03 g (0.1 mmol) of NiCl₂-Bipy followed by a THF (15 mL) solution of tri(4-bromophenyl)amine (4.8 g, 10 mmol). After stirring at room temperature for 4.5 hours, the solution was added to 300 mL of dichloromethane in a separatory funnel and was washed with water (2 x 500 mL). The organic layer, after drying and removal of solvent, gave a yellow oil which was dissolved in 80 mL of dichloromethane. The crude product was precipitated by adding the dichloromethane solution to 700 mL of hexane. Reworking the dichloromethane-hexane solution gave additional crude product. The combined crude product was heated to 150°C under reduced pressure (0.2 mm Hg) to remove bis-benzocyclobutene to give a yellow glassy solid (3.3 g). Liquid chromatography-mass spectrometry analysis of the product showed it to be a mixture of the following compositions.





5 Example 3 - Preparation of crosslinked polymer from a blend of oligomers from Examples 1 and 2

A blend of 4.05 g of the product from Example 1 and 0.45 g of the product from Example 2 was prepared by a solution process. The product and a film prepared as described in Example 1 were tested in the same manner as described in Example 1. The results were compiled in Table I. After heating a sample in a DSC cell from room temperature to 280°C at 3°C/minute and then at 280°C for 90 minutes, the blend was fully cured and the resulting polymer had a T_g of 242°C. The thin film prepared as described in Example 1 was then cured by heating to 280°C at 2.5°C/minute and at 280°C for 1 hour. The intensity of the absorption peak of the film was unaffected by exposure to xylenes and diminished by 2 percent after exposure to chloroform, thus demonstrating its solvent resistance. A film cured on the surface of a carbon electrode was analyzed by cyclic voltammetry. It showed an oxidation potential of +0.84 volt relative to Ag/AgCl and the cyclic voltammetry trace was reproducible through many redox cycles. This demonstrates the utility and durability of this polymeric film as a charge transport layer.

20 Example 4

A. Preparation of N,N-di(4-bromophenyl)-p-anisidine

A solution of N-bromosuccinimide (13.1 g, 72.6 mmol) in 50 mL of DMF was slowly added with stirring to a solution of N,N-diphenyl-p-anisidine (10.0 g, 36.3 mmol) in 50 mL of DMF. The rate of addition was such that the reaction temperature was kept below 50°C. The reaction was stirred for an additional 15 minutes after completion of addition. The reaction mixture was added to 200 mL of water in a separatory funnel. The mixture was extracted with hexane (250 mL). The organic layer was further washed with water

(2 x 200 mL) then dried over anhydrous MgSO_4 . The solvent was removed under reduced pressure to afford a slightly yellow oil which crystallized upon standing. Hexane (40 mL) was added to the flask and the contents were cooled to 4°C for 16 hours. The crystals were collected in a Buchner funnel, washed with hexane (3 x 25 mL) then dried in a vacuum oven at 60°C for 4 hours to afford 13.0 g (82 percent) of white crystals.

B. Preparation of crosslinkable oligomer from N,N-di(4-bromophenyl)-p-anisidine and bromobenzocyclobutene

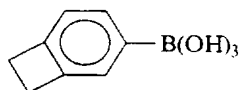
Example 1(B) was repeated using 1.95 g (7.5 mmol) of triphenylphosphine, 2.95 g (45 mmol) of zinc dust, 0.13 g (0.45 mmol) of $\text{NiCl}_2\cdot\text{Bipy}$, 6.5 g (15 mmol) of N,N-di(4-bromophenyl)-p-anisidine, 1.1 g (6 mmol) of BrBCB and 23 mL of DMAc. The reaction mixture was heated at 80°C for 17 hours and was then added to 150 mL of dichloromethane. The resulting solution was filtered to remove the unreacted zinc and concentrated. The concentrate was added to methanol to precipitate the crude product which was then refluxed in 300 mL of hexane and washed with more hot hexane (2 x 100 mL). After drying in a vacuum oven at 40°C for 4 hours, a pale yellow powder (4.41 g, 93 percent) was obtained. The product and a film prepared as described in Example 1(B) were tested in the same manner as described in Example 1(B). The results were compiled in Table I. These data demonstrated that crosslinking had no effect on the redox process and that the polymeric films were suitable for charge transport. The absorption peak of the cure film showed only a slight drop in intensity after exposure to xylenes and chloroform. This demonstrated the solvent resistance of the crosslinked polymer film.

Example 5

A. Preparation of 4-benzocyclobuteneboronic acid

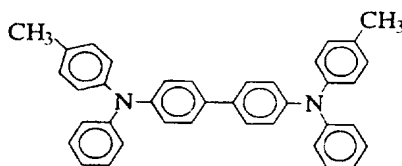
A dry reactor equipped with two addition funnels, nitrogen inlet, and a mechanical stirrer was set up over a dry ice bath. To one of the addition funnels was added a filtered, preformed Grignard reagent from the reaction of 4-bromobenzocyclobutene (18.3 g, 0.1 mol) with magnesium turnings (2.92 g, 0.12 mol) in THF (70 mL). To the other addition funnel was added trimethylborate (12.48 g, 0.12 mol) in THF (80 mL). The reactor was charged with 10 mL of the borate solution and was cooled to -70°C. 10 mL of the Grignard solution was then added. The remaining borate and Grignard solutions were then added in aliquots in such a way as to ensure a slight excess of borate. The reaction mixture was stirred at -70°C for one hour then stirred at room temperature for 20 hours. The reactor was cooled to 0°C and water (100 mL) was slowly added with vigorous stirring. The mixture was extracted with ether (400 mL). The ether layer was washed with water (2 x 200 mL), dried over anhydrous MgSO_4 , then concentrated on a roto-evaporator to afford a light-tan-colored solid (22.0 g,

87 percent). ^1H and ^{13}C NMR spectra were consistent with the following structure.



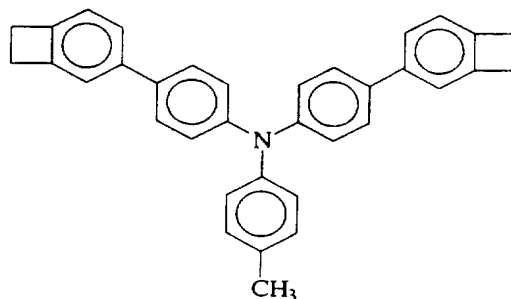
5 B. Preparation of N,N-Di-(4-bromophenyl)-p-tolylamine

To a stirred solution of N,N'-diphenyl-p-tolylamine (99.7 g, 0.38 mol) in DMF (300 mL) was slowly added a solution of N-bromosuccinimide (138.2 g, 0.78 mol) in DMF (300 mL) while maintaining a reaction temperature of less than 50°C. The reaction solution was concentrated under reduced pressure, then was added to 300 mL of water to precipitate the product. The gray-colored solid was recrystallized in ethanol to afford off-white crystals. The crystals were collected and dried in a vacuum oven overnight to afford 135.4 g (85 percent). ^1H and ^{13}C NMR spectra were consistent with the structure of the desired product as follows.



15 C. Coupling of 4-benzocyclobuteneboronic acid with N,N'-di-(4-bromophenyl)-p-tolylamine

To a reactor was added N,N'-di-(4-bromophenyl)-p-tolylamine (4.17 g, 0.01 mol), 2N aqueous sodium carbonate solution (10 mL), 4-benzocyclobuteneboronic acid (5.92 g, 0.04 mol), toluene (20 mL), and ethanol (20 mL). The reactor was purged with nitrogen for 10 minutes, then to it was added tetrakis(triphenylphosphine)-palladium (0) (0.4 g). The reaction mixture was heated to gentle reflux for 20 hours with vigorous stirring. The reaction mixture was added to a separatory funnel together with 100 mL of water. The mixture was extracted with ether (2 x 250 mL). The combined ether layer was washed with 3N NaOH solution (2 x 150 mL), water (2 x 150 mL), dried over anhydrous MgSO_4 , then concentrated on a roto-evaporator. The product was purified by silica gel flash column chromatography with hexane to afford a white solid (2.2 g). ^1H and ^{13}C NMR spectra were consistent with the following structure.

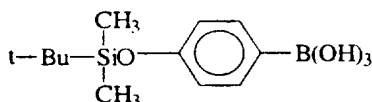


A homogeneous film of the material was obtained by spin-coating from a toluene solution at 2500 rpm for 90 seconds. The film was cured according to the following schedule: Nitrogen purge at ambient temperature for 30 minutes; heated to 250°C at the rate of 3°C/minute; held at 250°C for 2 hours; cooled to ambient temperature. The cured film examined under the microscope showed that the film had puddled. A 1.5-g sample of the material was B-staged under vacuum at 190°C for 3 hours. DSC analysis of the B-staged material showed that 40 percent of the BCB units had reacted. A film of the B-staged material spin-coated from toluene solution had the same UV absorption as that of the monomer. The photoluminescent spectra were taken of the film from the B-staged oligomer and the B-staged oligomer in chloroform. The film was then cured according to the above cure schedule. Analysis of the film by microscope showed that the integrity of the film was maintained and no puddle effect was seen. The cured film was resistant to chloroform.

Example 6

A. Preparation of 4-(t-butyltrimethylsilyloxy)-bromobenzene

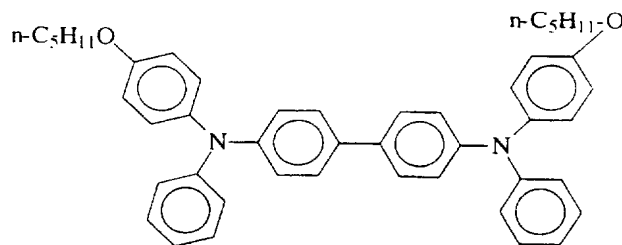
The process described in Example 5A was performed with a preformed Grignard reagent from the reaction of 4-(t-butyltrimethylsilyloxy)-bromobenzene (28.7 g, 0.1 mol) with magnesium turnings (2.96 g, 0.12 mol) in THF (70 mL) and trimethylborate (12.5 g, 0.12 mol) in THF (80 mL). To recover the product, the reactor was cooled to 0°C and water (50 mL) was slowly added with vigorous stirring. The reaction was neutralized with aqueous H₂SO₄, and was extracted with ether (2 x 300 mL). The ether layer was washed with water (2 x 150 mL), dried over anhydrous MgSO₄, then concentrated on a roto-evaporator to afford an off-white color solid (14.22 g, 96 percent). ¹H and ¹³C NMR spectra were consistent with the following structure.



B. Preparation of N,N'-diphenyl-N,N'-di-(4-pentoxypentyl)benzidine

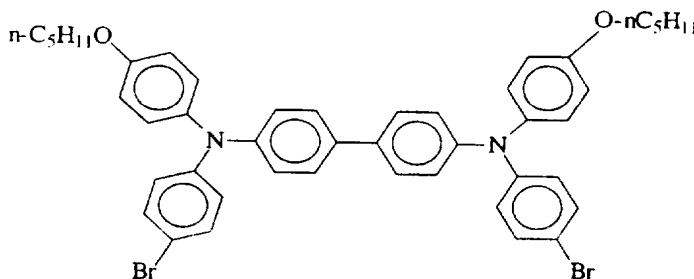
To a reactor was added N,N'-diphenylbenzidine (13.5 g, 0.04 mol), 4-iodophenylpentylether (29.0 g, 0.1 mol), copper bronze powder (8.9 g, 0.14 mol), powdered potassium carbonate (38.5 g, 0.28 mol), 18-crown-6-ether (1.8 g, 0.007 mol), and 1,2-dichlorobenzene (100 mL). With a slow purge of nitrogen through the condenser, the stirred reaction was heated to 180°C for 90 hours. The hot reaction mixture was filtered through a bed of filter aid and the filtrate was concentrated under reduced pressure to afford a dark brown viscous liquid which was purified by silica gel flash column chromatography (25 percent toluene in hexane as eluent) to give 25.1 g (95 percent) of a white solid. ¹H and

¹³C NMR spectra were consistent with the following structure.



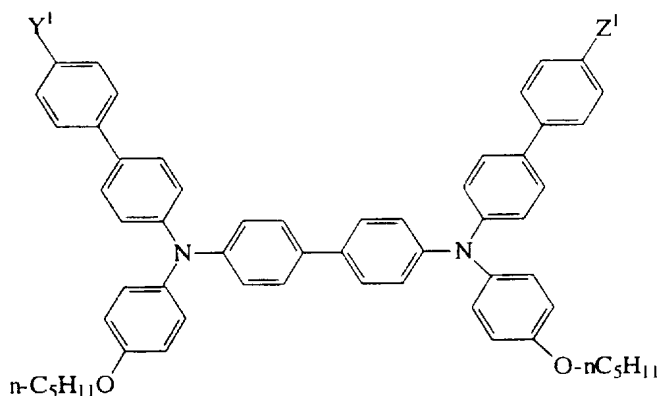
C. Preparation of N,N'-di-(4-bromophenyl)-N,N'-di-(4-pentoxyphenyl)benzidine

To a stirred solution of N,N'-diphenyl-N,N'-di-(4-pentoxyphenyl)benzidine (24.9 g, 0.038 mol) in DMF (200 mL) was slowly added a solution of N-bromosuccinimide (13.4 g, 0.076 mol) in DMF (100 mL). The reaction solution was concentrated under reduced pressure and then added to 50 percent aqueous ethanol, precipitating out a grayish solid which was collected and dried in a vacuum oven at ambient temperature overnight. The yield was 30.6 g (99 percent). ¹H and ¹³C NMR spectra were consistent with the following structure.



D. Coupling of 4-(t-butyl-dimethylsilyloxy)-benzeneboronic acid with N,N'-di-(4-bromophenyl)-N,N'-di-(4-pentoxyphenyl)benzidine

The procedure of Example 5(C) was repeated with the following reagents: N,N'-di-(4-bromophenyl)-N,N'-di-(4-pentoxyphenyl)benzidine (8.2 g, 0.01 mol), 2*N* aqueous sodium carbonate solution (10 mL), toluene (20 mL), tetrakis(triphenyl-phosphine)-palladium (0) (0.4 g), and 4-(t-butyl-dimethylsilyloxy)benzeneboronic acid (7.6 g, 0.03 mol). The reaction mixture was added to a separatory funnel, together with 100 mL of water. The mixture was extracted with ether (400 mL). The ether layer was washed with 3*N* NaOH solution (150 mL), water (2 x 300 mL), dried over anhydrous MgSO₄, then concentrated on a roto-evaporator to afford a brown oil. High pressure liquid chromatographic (HPLC) analysis indicated a minor and two major components. Based on mass spectrometry analysis, the proposed structures of the three components were as follows:



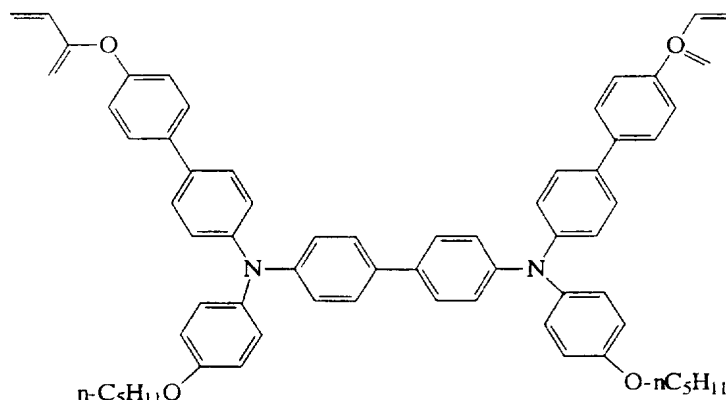
wherein Y' and Z' are OH and OSi(CH₃)₂C(CH₃)₃, respectively, in 42 percent of the compounds; Y' and Z' are (CH₃)₃CsSi(CH₃)₂O and OSi(CH₃)₂C(CH₃)₃, respectively, in 50 percent of the compounds; and Y' and Z' are OH in 3 percent of the compounds.

5 Example 7 - Preparation of N,N'-di-4(4'-hydroxybiphenyl)-N,N'-di-(4-pentoxyphenyl)benzidine

The crude reaction product from Example 6(D) was dissolved in 100 mL of 2 percent HCl in THF solution. The solution was stirred at ambient temperature for four days. Reaction solution was added to 300 mL of ether in a separatory funnel then washed with water (2 x 150 mL), saturated NaHCO₃ solution (150 mL), then again with water (2 x 150 mL). The ether layer was dried over anhydrous MgSO₄ then concentrated on a roto-evaporator to afford 10.5 g of a dark-brown, viscous liquid with some crystals. The product was isolated by flash column chromatography over silica gel with 5 percent (v/v) ethyl acetate in toluene to afford 6.0 g of light-brown crystals (71 percent based on N,N'-di-(4-bromophenyl)-N,N'-di-(4-pentoxyphenyl)-benzidine). ¹H and ¹³C NMR spectra were consistent with the di-4(4'-hydroxybiphenyl) structure shown above, wherein Y' and Z' are OH.

15 Example 8 - Diacrylate of N,N'-di-4(4'-hydroxybiphenyl)-N,N'-di-(4-pentoxyphenyl)-benzidine

A solution of acryloyl chloride (0.52 g, 5.6 mmol) in 5.0 mL of methylene chloride was slowly added to a solution of N,N'-di-4(4'-hydroxybiphenyl)-N,N'-di-(4-pentoxyphenyl)benzidine (2.0 g, 2.4 mmol) and triethylamine (0.95 g, 95 mmol) in 20 mL of methylene chloride. The solution was stirred at ambient temperature for 10 minutes. Crude reaction solution was concentrated under reduced pressure to dryness then redissolved in 200 mL of ether. The ether solution was washed with water (3 x 150 mL), dried over anhydrous MgSO₄, and concentrated on the roto-evaporator to afford a yellow, glassy solid. The glassy solid was dissolved in a minimum amount of toluene. The toluene solution was added to methanol, precipitating a yellow solid. The precipitate was collected and dried in a vacuum oven overnight to afford a pale yellow solid (2.0 g, 87 percent). ¹H and ¹³C NMR spectra were consistent with the following structure.



DSC analysis showed a sharp endothermic peak at 74°C corresponding to melting and a broad exothermic peak starting at 200°C with a maximum at 261°C, and a small exothermic transition at 160°C. DSC rescan of the sample showed no transition up to 325°C.

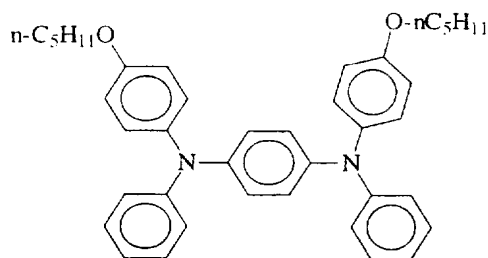
Cyclic voltammogram of the product (0.2M tetrabutylammonium perchlorate in dichloromethane, referenced to Ag/AgCl electrode) indicated an $E_{1ox} = +0.61V$ (rev) and $E_{2ox} = +0.80V$ (rev). A film of the material was obtained by spin-coating from toluene solution. It had a strong UV absorption (λ_{max} 364 nm) and a photoluminescence peak at 425 nm. A film cured in nitrogen for 8 hours at 185°C showed absorption and photoluminescence behavior identical to those of an uncured film.

The diacrylate was blended with 1.5 weight percent of 2,2-dimethoxy-2-phenylacetophenone and 7.5 weight percent of trimethylolpropane triacrylate in toluene to afford a 2 percent (wt/v) solution. Films were cured in a UVP mid-range ultraviolet crosslinker model CL-1000 for 15 minutes at 200 mJ/cm². The cured film was resistant to toluene. Cyclic voltammogram of the cured film indicated an $E_{1ox} = +0.70V$ (rev); $E_{2ox} = +0.77V$ (rev).

Example 9

A. Preparation of N,N'-diphenyl-N,N'-di-(4-pentoxyphenyl)-1,4-phenylenediamine

The procedure of Example 6(B) was repeated with the following reagents: N,N'-diphenyl-1,4-phenylenediamine (11.0 g, 0.04 mol), 4-iodophenylpentylether (29.0 g, 0.1 mol), copper bronze powder (8.9 g, 0.14 mol), potassium carbonate (38.5 g, 0.28 mol), 18-crown-6-ether (1.8 g, 0.007 mol), and 1,2-dichlorobenzene (100 mL). After 72 hours, the hot reaction mixture was filtered through a bed of filter aid and concentrated under reduced pressure to afford dark-brown, viscous liquid which was percolated through a bed of silica gel with hexane to remove some of the color. Recrystallization from ethanol/acetone afforded 19.3 g (60 percent) of a tan-colored solid. ¹H and ¹³C NMR spectra were consistent with the following structure.

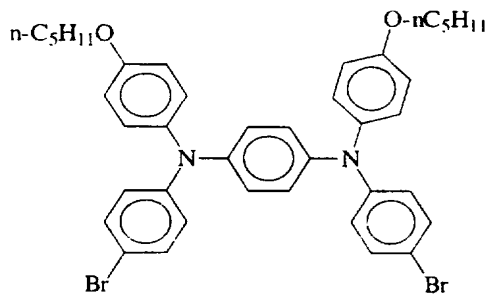


Cyclic voltammogram of the product (0.2M tetrabutylammonium perchlorate in dichloromethane, referenced to Ag/AgCl electrode) indicated reversible oxidation potentials of +0.39V and +0.84V.

5 B. Preparation of N,N'-di-(4-bromophenyl)-N,N'-di-(4-pentoxyphenyl)-1,4-phenylenediamine

The procedure of Example 5(B) was repeated with the following reagents: N,N'-diphenyl-N,N'-di-(4-pentoxyphenyl)-1,4-phenylenediamine (14.0 g, 0.024 mol) in THF (150 mL), N-bromosuccinimide (9.0 g, 0.051 mol), and DMF (100 mL). Three recrystallizations of the crude product from acetone gave tan-colored crystals (10.8 g, 60 percent). ¹H and

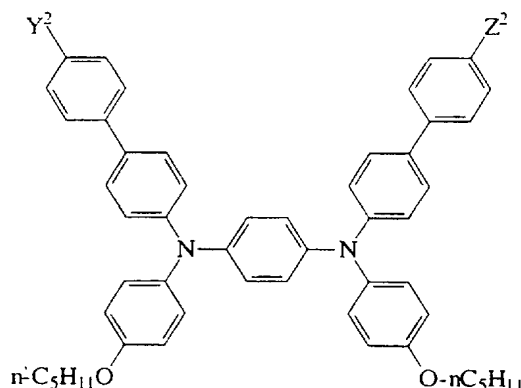
10 ¹³C NMR spectra were consistent with the following structure.



C. Coupling of 4-(t-butyldimethylsilyloxy)benzeneboronic acid with N,N'-di-(4-bromophenyl)-N,N'-di-(4-pentoxyphenyl)-1,4-phenylenediamine

The procedure of Example 5(C) was repeated with the following reagents: N,N'-di-(4-bromophenyl)-N,N'-di-(4-pentoxyphenyl)-1,4-phenylenediamine (7.4 g, 0.01 mol), 2N aqueous sodium carbonate solution (10 mL), toluene (20 mL), tetrakis(triphenyl-phosphine)-palladium (0) (0.4 g), and 4-(t-butyldimethylsilyloxy)-benzeneboronic acid (7.6 g, 0.03 mol). The same work-up procedure afforded a brown oil (10.2 g). HPLC analysis of the crude product indicated three components. Based on the mass spectrometry analysis, the proposed structure of the three components were as follows:

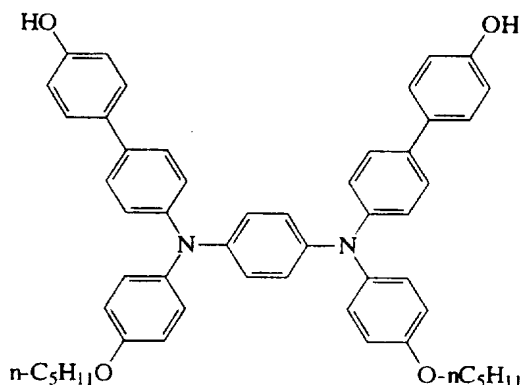
20



wherein Y^2 and Z^2 are $(CH_3)_3Si(CH_3)_2O$ and $OSi(CH_3)_2C(CH_3)_3$, respectively, in 28 percent of the compounds; Y^2 and Z^2 are OH and $OSi(CH_3)_2C(CH_3)_3$, respectively, in 47 percent of the compounds; and Y^2 and Z^2 are OH in 20 percent of the compounds.

5 Example 10 - Preparation of N,N'-di-4(4'-hydroxybiphenyl)-N,N'-di-(4-pentoxyphenyl)-1,4-phenylenediamine

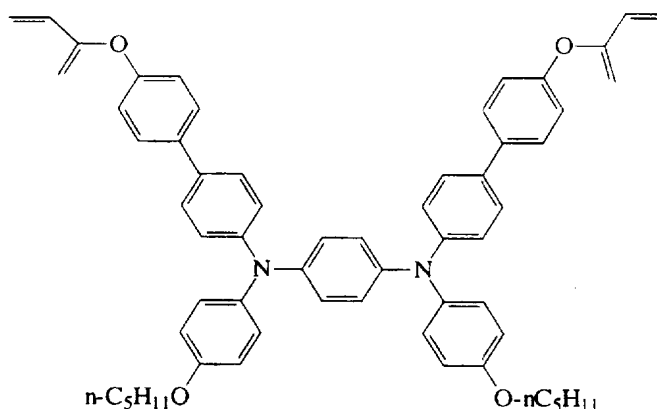
The crude reaction product from Example 9 was dissolved in 100 mL of 5 percent HCl in THF solution. The solution was stirred at ambient temperature for 23 hours. Reaction solution was added to 300 mL of ether in a separatory funnel then washed with water
 10 (2 x 150 mL), saturated $NaHCO_3$ solution (150 mL), then again with water (2 x 150 mL). The ether layer was dried over anhydrous $MgSO_4$ then concentrated on a roto-evaporator to afford a dark-brown, viscous liquid with some crystals. Product was isolated by flash column chromatography over silica gel with 7 percent (v/v) ethyl acetate in toluene to afford 3.5 g of light-brown crystals (46 percent base on N,N'-di-(4-bromo-phenyl)-N,N'-di-(4-pentoxyphenyl)-
 15 1,4-phenylenediamine; low yield was mostly due to loss from spillage). 1H and ^{13}C NMR spectra were consistent with the following structure.



Example 11 - Preparation of a diacrylate of N,N'-di-4(4'-hydroxybiphenyl)-N,N'-di-(4-pentoxyphenyl)-1,4-phenylenediamine

20 Example 8 was repeated with the following reagents: acryloyl chloride (0.50 g, 5.5 mmol) in 5.0 mL of methylene chloride, N,N'-di-4(4'-hydroxybiphenyl)-N,N'-di-(4-

pentoxyphenyl)-1,4-phenylenediamine (1.7 g, 2.2 mmol), and triethylamine (0.90 g, 90 mmol) in 20 mL of methylene chloride. ^1H and ^{13}C NMR spectra were consistent with the following structure.



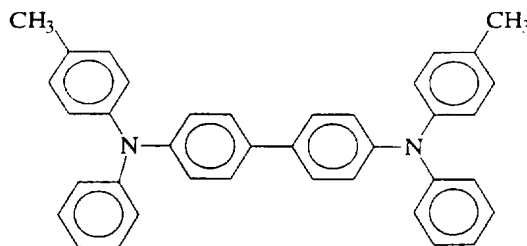
DSC analysis showed a sharp endothermic peak at 170°C due to melting and a broad exothermic peak starting at 225°C with a maximum at 279°C. DSC rescan of the sample showed no transition up to 300°C. Cyclic voltammogram of the product (0.2M tetrabutylammonium perchlorate in dichloromethane, referenced to Ag/AgCl electrode) indicated $E_{1ox} = +0.40\text{V}$ and $E_{2ox} = +0.82\text{V}$.

The diacrylate was blended with 1.5 weight percent of 2,2-dimethoxy-2-phenylacetophenone and 7.5 weight percent of trimethylolpropane triacrylate in toluene to afford a 2 percent (wt/v) solution. Films were cured in a UVP mid-range ultraviolet crosslinker model CL-1000 for 15 minutes at 200 mJ/cm². The cured film was resistant to toluene.

Example 12

A. Preparation of N,N'-diphenyl-N,N'-di-(4-methylphenyl)benzidine

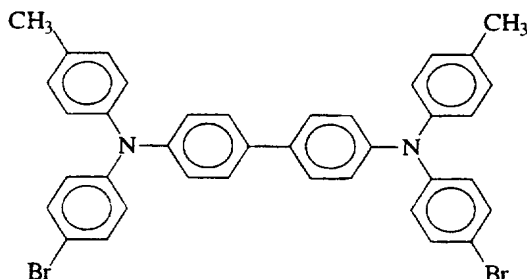
The procedure of Example 6(B) was repeated with the following reagents: N,N'-diphenyl-1,4-phenylenediamine (4.85 g, 0.014 mol), 4-iodotoluene (9.43 g, 0.043 mol), copper bronze powder (3.8 g, 0.06 mol), potassium carbonate (16.6 g, 0.12 mol), 18-crown-6-ether (0.78 g, 0.003 mol), and 1,2-dichlorobenzene (50 mL). After 40 hours, the hot reaction mixture was filtered through a bed of filter aid and the filtrate was concentrated under reduced pressure to afford a dark-brown oil which became a semi-solid upon standing. The product was purified by silica gel flash column chromatography with 10 percent toluene in hexane to yield a white solid (5.75 g, 77 percent). ^1H and ^{13}C NMR spectra were consistent with the following structure.



A cyclic voltammogram of the product, carried out as described in Example 9(A), indicated reversible oxidation potentials of +0.68V and +0.81V.

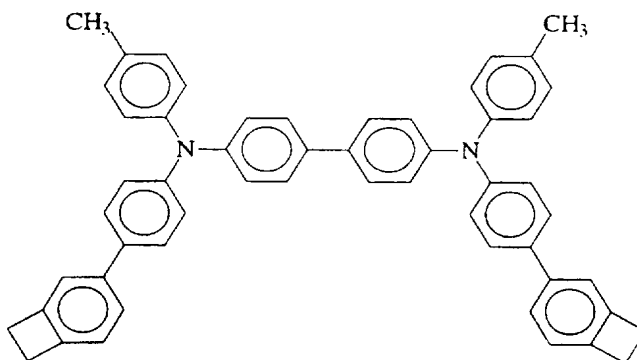
B. Preparation of N,N'-di-(4-bromophenyl)-N,N'-di-(4-methylphenyl)benzidine

- 5 To a stirred solution of N,N'-diphenyl-N,N'-di-(4-methylphenyl)benzidine (5.7 g, 0.001 mol) in THF (15 mL) and DMF (10 mL) was slowly added (15 minutes) a solution of N-bromosuccinimide (4.0 g, 0.001 mol) in DMF (10 mL). The reaction solution was concentrated under reduced pressure and then added to 10 percent aqueous ethanol, precipitating out a white solid. The white solid was collected and dried in a vacuum oven
- 10 overnight to afford 6.7 g (91 percent). ^1H and ^{13}C NMR spectra were consistent with the following structure.



C. Coupling of 4-benzocyclobuteneboronic acid with N,N'-di-(4-bromophenyl)-N,N'-di-(4-methylphenyl)benzidine

- 15 Example 5(C) was repeated with N,N'-di-(4-bromophenyl)-N,N'-di-(4-methylphenyl)benzidine (3.3 g, 0.005 mol), toluene (20 mL), 2N aqueous sodium carbonate solution (10 mL), tetrakis(triphenylphosphine)-palladium (0) (0.175 g) and 4-benzocyclobuteneboronic acid (3.0 g, 0.02) dissolved in a minimum amount of ethanol. The product was a white solid (2.0 g). ^1H and ^{13}C NMR spectra were consistent with the following structure.



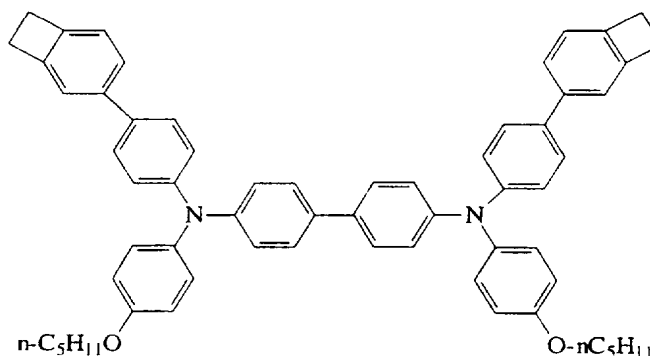
The material in the solid state had a strong UV absorption (I_{\max} 336 nm) and a photoluminescence peak at 419 nm. Cyclic voltammogram of the product (0.2M tetra-butylammonium perchlorate in dichloromethane, referenced to Ag/AgCl electrode) indicated an $E_{1ox} = +0.63V$ (rev) and $E_{2ox} = +0.83V$ (rev).

A film of the material was obtained by spin-coating from a toluene solution (2500 rpm for 90 seconds). The film was cured according to the schedule in Example 5(C). The cured film examined under the microscope showed that the resin had formed puddles during cure. A 1.5 g sample of the material was B-staged under vacuum at 190°C for 3 hours. DSC analysis of the B-staged material showed that 36 percent of the BCB units had reacted. A film of the B-staged material spin-coated from toluene solution was cured according to the schedule in Example 5(C). Analysis of the film by microscope showed a uniform film without puddles. The cured film was resistant to chloroform. Cyclic voltammogram of the cured film had an $E_{1ox} = +0.75V$ (rev); $E_{2ox} = +0.86V$ (rev). The cured film had a UV absorption with I_{\max} 333 nm.

Example 13 - Coupling of 4-benzocyclobuteneboronic acid with N,N'-di-(4-bromophenyl)-N,N'-di-(4-pentyloxyphenyl)benzidine

Example 5(C) was repeated with N,N'-di-(4-bromophenyl)-N,N'-di-(4-pentyloxyphenyl)benzidine (4.9 g, 0.006 mol) (example 18), toluene (20 mL), 2N aqueous sodium carbonate solution (10 mL), tetrakis(triphenylphosphine)-palladium (0) (0.175 g) and 4-benzocyclobuteneboronic acid (3.0 g, 0.02 mol). The product was a dark-brown, glassy solid. The solid was redissolved in 200 mL of toluene. To the toluene solution was added 100 mL of water and 50 mL of ethylenediamine. The mixture was heated to 60°C with vigorous stirring for 2.5 hours. The aqueous layer was removed and the toluene layer was washed with water (2 x 150 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The product was isolated by flash column chromatography on silica gel.

¹H and ¹³C NMR spectra were consistent with the following structure.



The material in the solid state had a strong UV absorption (I max 367 nm) and a solution (chloroform) absorption of 364 nm. The material in the solid state had a

5 photoluminescent peak at 423 nm and a solution (chloroform) emission at 421 nm. DSC analysis of the product showed a sharp endothermic peak at 72°C corresponding to melting and a broad exothermic peak starting at 190°C with a maximum at 259°C corresponding to curing reaction of BCB. DSC rescan of the sample showed a glass transition at 275°C.

10 The material was B-staged under vacuum at 190°C for 3 hours. DSC analysis of the B-staged material showed a Tg of 97°C and that 36 percent of the BCB units had reacted. A film of the B-staged material spin-coated from toluene solution was cured according to the schedule in Example 5(C). Analysis by microscope showed a smooth and homogeneous film whose photoluminescent spectrum showed a broad emission at 489 nm.

Table I

Example	1	4	3	5
Ratio ¹	4.7	4.9	2.8	
Uncured Polymer				
DSC Peak °C ²	200/261	210/260	200/257	
UV Absorption Peak nm	364	366		331/246
Photoluminescent Peak nm	420	422		423
Oxidation Potential Volt	+0.60/ +0.88	+0.59/ +0.81		+0.76
Cured film				
UV Absorption Peak nm	354	358	345	331 ⁴
Photoluminescent Peak nm ³	490/420	490/422	492/422	433/460 ² 419 ⁵
Oxidation Potential Volt	+0.61/ +0.88	+0.61/ +0.89	+0.84	+0.86 ⁶

1. Ratio of tertiary amine to haloaromatic compound.

2. Beginning of peak/peak maximum.

3. Major peak/minor peak.

4. Film from B-staged oligomer, 40 percent cured.

5. B-staged oligomer in chloroform.

6. Film from B-staged material which is finally cured.

Example 14 - Preparation of 4,4',4''-tris[N-(3-methoxyphenyl)-N-phenylamino]tri-phenylamine

Tri(4-iodophenyl)amine was prepared according to the procedure described by T. N. Baker et. al. in Journal of Organic Chemistry, Vol. 30, p. 3714 (1965). A mixture of tri(4-iodophenyl)amine (24.8 g, 40 mmol), copper powder (18.0 g, 288 mmol), powdered K₂CO₃ (69.0 g, 500 mmol), 18-crown-6 (3.2 g, 12 mmol), and 3-methoxydiphenylamine (28.0 g, 140 mmol) in 1,2-dichlorobenzene (150 mL) was heated with stirring at 185°C for 3 days. The water generated by the reaction was removed by a slow stream of nitrogen. The content of the reactor was filtered and the filter cake washed with toluene. The combined organic solution was poured into methanol to precipitate a dark pasty solid which

was purified by column chromatography (silica gel, 1:1 toluene:hexane). From the fractions collected were obtained 12 g of the desired branched-amine having a melting point (m.p.) of 185°C, reversible oxidation potential in CH_2Cl_2 : 0.30 and 0.61 volt and 4.3 g of 4,4'-bis[N-(3-methoxyphenyl)-N-phenylamino]triphenylamine (m.p. 172°C), reversible oxidation potential in CH_2Cl_2 : 0.41 and 0.73 volt. The identities of these materials were confirmed by mass spectrometry, ^1H , and ^{13}C NMR.

Example 15 - Preparation of 4,4',4''-tris[N-(3-methoxyphenyl)-N-phenylamino]tri-phenylamine

The procedure described in Example 14 was carried out using a mixture of tri(4-iodophenyl)amine (31.0 g, 50 mmol), copper powder (19.1 g, 300 mmol), powdered K_2CO_3 (69.0 g, 500 mmol), 18-crown-6 (2.6 g, 10 mmol), 3-methoxydiphenylamine (29.9 g, 150 mmol) in 150 mL 1,2-dichlorobenzene, which was heated with stirring at 185°C for 19 hours. Working up the crude product in the same manner yielded 7.0 g of 4,4'-bis[N-(3-methoxyphenyl)-N-phenylamino]triphenylamine and 19.7 g of 4,4',4''-tris[N-(3-methoxyphenyl)-N-phenylamino]triphenylamine (47.0 percent).

Example 16 - Preparation of 4,4',4''-tris[N-(3-methoxyphenyl)-N-phenylamino]tri-phenylamine

A 500-mL, three-necked, round-bottomed flask, equipped with an overhead stirrer, a nitrogen line and a reflux condenser, was charged with palladium acetate (269 mg, 1.2 mmol), tri-*o*-tolylphosphine (804 mg, 2.6 mmol), and toluene (30 mL). The mixture was stirred at ambient temperature (25°C) for 10 minutes until a homogenous yellow solution was formed. To this solution was added tri-(4-bromophenyl)amine (9.64 g, 20.0 mmol), 3-methoxydiphenylamine (13.17 g, 66.1 mmol), sodium tert-butoxide (6.35 g, 66.1 mmol) and more toluene (220 mL). With a slow purge of nitrogen through the condenser, the reaction vessel was placed into an oil bath and the stirred reaction was heated to reflux for 14 hours. The oil bath was removed and the reaction mixture was cooled to ambient temperature. To the stirred mixture concentrated hydrochloric acid (7 mL) was added and the stirring was continued for 20 minutes. The mixture was filtered through an alumina (neutral) bed on a fritted funnel and rinsed with toluene. Removal of the solvent on a rotary evaporator under reduced pressure afforded an orange-brown viscous oil. Chromatography on a silica gel column (7.5 x 35 cm, 50 percent toluene/hexane as eluent) provided 12.8 g of light-yellow thick oil. Recrystallization from hexane/toluene afforded 10.9 g (65 percent) of fine pale-yellow solids. The product was further purified by stirring in acetone (150 mL) for 4 hours. It is then collected by filtration and dried in a vacuum oven overnight to give 10.7 g of pale-yellow fine powder.

Example 17 - Preparation of 4,4',4''-tris[N-(3-hydroxyphenyl)-N-phenylamino]tri-phenylamine

A mixture of the tri-methyl ether prepared in Example 16 (4.0 g, 4.8 mmol) and pyridine hydrochloride (40 g) was heated under nitrogen with stirring at 210°C for 2.5 hours.

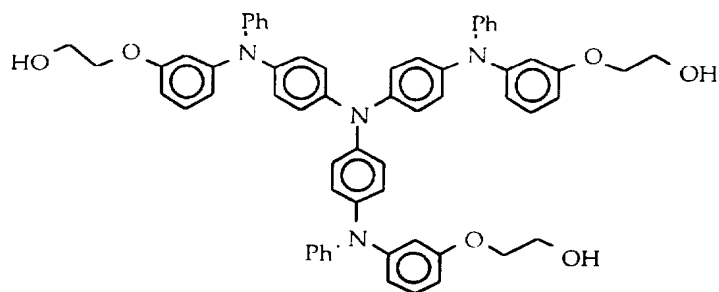
The reaction mixture was then cooled to 140°C and to it was added 600 mL of cold water over 10 minutes with stirring. The resulting green solid was collected by filtration, washed with water and recrystallized from 1:1 isopropyl alcohol:water to provide 3.5 g (92 percent) of the corresponding trisphenol having a m.p. of 157°C to 159°C.

5 Example 18 - Preparation of 4,4',4''-tris[N-(3-hydroxyphenyl)-N-phenylamino]tri-phenylamine

A 1-L three-necked, round-bottomed flask, equipped with an overhead stirrer and an air condenser connected to a nitrogen line, was charged with 4,4',4''-tris[N-(3-methoxyphenyl)-N-phenylamino]triphenylamine (9.0 g, 10.7 mmol), and pyridine hydrochloride (135 g). With a slow purge of nitrogen through the condenser, the reaction vessel was placed in an oil bath and the mixture was stirred and heated to 220°C. At 150°C a homogenous yellow solution was formed. The progress of the reaction was monitored by high pressure liquid chromatography (HPLC) analysis. The reaction took 6 hours and during the time the solution turned gradually to dark green. The mixture was allowed to cool to 140°C and 600 mL of water was added. The mixture was then stirred at ambient temperature for 2 hours. The product was collected by filtration, washed with water and dried in a vacuum oven at 45°C overnight to provide 8.3 g (97 percent) of pale-green powdered material. HPLC analysis indicated the product was less than 99 percent purity. The results of ¹H NMR and ¹³C NMR analyses were consistent with the expected structure.

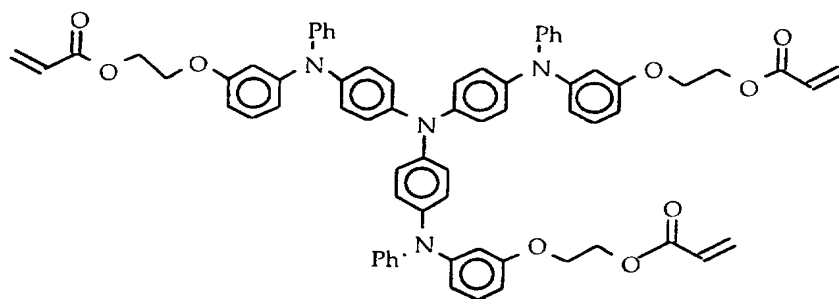
15 Example 19 - Preparation of 4,4',4''-tris[N-(3-(2-hydroxyethyloxy)phenyl)-N-phenyl-
20 amino]triphenylamine

A 500-mL round-bottomed flask equipped with an overhead stirrer, a nitrogen line, and a reflux condenser, was charged with the trisphenol produced in Example 18 (6.0 g, 6.5 mmol), 2-bromoethanol (8.5 g, 68.0 mmol), powdered potassium carbonate (12.5 g, 90.2 mmol) and DMF (200 mL). The mixture was stirred and heated to reflux for 4 hours. Most solvent was removed on a rotary evaporator under reduced pressure, and the product was precipitated by the slow addition of dilute aqueous hydrochloric acid (10 percent, 50 mL). The product was collected by filtration, washed with water and dried in a vacuum oven at 45°C overnight to provide 6.5 g (93 percent) of greenish fine solid. HPLC analysis indicated the product was in less than 99 percent purity. The results of ¹H NMR and ¹³C NMR of the product were consistent with the expected structure:



Example 20 - Preparation of 4,4',4''-tris[N-(3-(2-acryloyloxyethoxy)phenyl)-N-phenyl-amino]-triphenylamine

A 250-mL, three-necked, round-bottomed flask equipped with a magnetic stirrer, a nitrogen line, and an ice bath was charged with the triol obtained in Example 19 (6.0 g, 6.5 mmol), triethylamine (4.2 g, 41.4 mmol) and methylene chloride (150 mL). The mixture was stirred and cooled to 0°C. With a slow purge of nitrogen through the system, a solution of acryloyl chloride (3.76 g, 41.4 mmol) in methylene chloride (15 mL) was added dropwise. The ice bath was removed and the reaction was then stirred at ambient temperature for 15 minutes. The reaction was quenched with the addition methanol (5 mL) and the mixture was transferred to a separatory funnel, washed with brine (20 percent, 2 x 50 mL) and dried with magnesium sulfate. After filtering, the solvent was evaporated on a rotary evaporator under reduced pressure. The residual oil was chromatographed on a silica gel column (3 x 25 cm) eluted with methanol (1 percent)/methylene chloride. The product containing fractions were combined and the solvent was removed on a rotary evaporator to afford 2.6 g (24 percent) of amorphous solid. ¹H NMR and ¹³C NMR were consistent with the expected structure:



Example 21 - Preparation of 4,4',4''-tris[N-(3-(benzyloxy)phenyl)-N-phenyl-amino]-triphenylamine

A 50-mL, three-necked, round-bottomed flask, equipped with a magnetic stirrer, a reflux condenser which was connected to a nitrogen line, was charged with the triphenol from Example 17 (500 mg, 0.6 mmol), benzyl chloride (1.08 g, 8.5 mmol), tetrabutylammonium hydroxide (1 M in methanol, 8.5 mL, 8.5 mmol) and toluene (15 mL). With a slow

purge of nitrogen through the condenser, the reaction vessel was placed in an oil bath and the stirred reaction was heated to 60°C for 24 hours. During this time, the original green solution turned to tan. The reaction was diluted with more toluene (25 mL), washed with water (3 x 15 mL), and dried with sodium sulfate, and the solvent was evaporated on a rotary evaporator under reduced pressure. The solvent residue was further removed on a Kugelrohr apparatus to afford a dark-brown oil. Flash chromatography on a silica gel column (2.5 cm x 30 cm) eluted with 50 percent hexane/toluene provided 490 mg of light-yellow viscous oil. Recrystallization from benzene/hexane afforded 441 mg (66 percent) of product as a pale-yellow powder. ¹H NMR and ¹³C NMR were consistent with the expected structure.

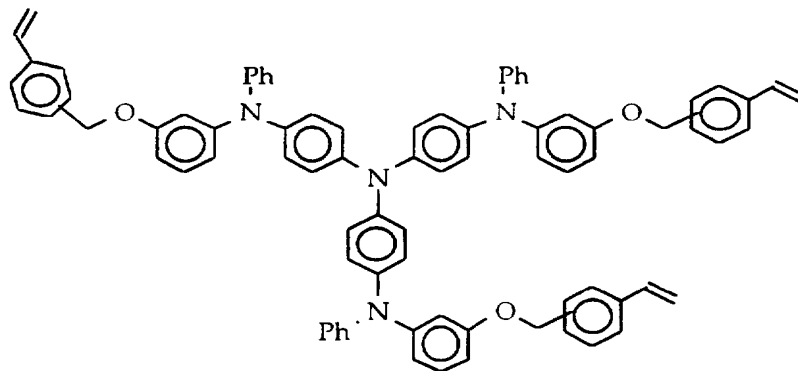
Reversible oxidation potentials in CH₂Cl₂ were 0.46 and 0.69 volt.

Example 22 - Preparation of 4,4',4''-tris[N-(3-(benzyloxyphenyl)-N-phenylamino]triphenylamine

The above experiment was repeated with 79.5 mg of trisphenol, 276 mg of potassium carbonate, 253 mg of benzyl chloride, 100 mg of benzyltriethyl ammonium chloride and 5 mL of dimethylformamide. The mixture was stirred at 70°C to 75°C for 1 hour and was then diluted with water (50 mL). The product was extracted with ether and recrystallized from benzene-hexane to give an off-white solid (72 mg), m.p. 80°C to 82°C. ¹H NMR and ¹³C NMR were consistent with the expected structure.

Example 23 - Preparation of 4,4',4''-tris[N-(3-(vinylbenzyloxyphenyl)-N-phenylamino]triphenylamine

The above example was repeated with vinylbenzyl chloride in place of benzyl chloride. The desired product was purified by passing through an alumina column followed by recrystallization from benzene-hexane. The yield was 64 percent. Differential scanning calorimetry (DSC) showed two endothermic transitions at 168°C and 195°C, followed by an exothermic transition at 253°C. ¹H NMR and ¹³C NMR were consistent with the expected structure:



Example 24 - Alkylation of 4,4'4''-tris[N-(3-(2-hydroxyethyloxy)phenyl)-N-phenyl-amino]-triphenylamine with a mixture of benzyl chloride and vinylbenzyl chloride

A 50-mL, three-necked, round-bottomed flask, equipped with a magnetic stirrer, a reflux condenser and a nitrogen line, was charged with the trisphenol from Example 18 (1.0 g, 1.3 mmol), benzyl chloride (2.2 g, 1.7 mmol), vinylbenzyl chloride (2.7 g, 17 mmol), tetrabutylammonium hydroxide (1 M in methanol, 22.0 mL, 22.0 mmol) and toluene (30 mL). With a slow purge of nitrogen through the condenser, the reaction vessel was placed in an oil bath and the stirred reaction was heated to 60°C for 28 hours. The reaction was diluted with more toluene (30 mL), washed with water (3 x 20 mL), and dried with sodium sulfate. After filtration, the solvent was evaporated on a rotary evaporator under reduced pressure, and the solvent residue was further removed on a Kugelrohr apparatus to afford a dark-brown oil. Flush chromatography on a silica gel column (2.5 x 30 cm) eluted with 50 percent hexane/toluene provided 1.03 g of light-yellow viscous oil. Recrystallization from benzene/hexane afforded 740 mg of product as a pale-yellow powder. ¹H NMR analysis indicated the product contains 1.48 unit of benzyl ether and 1.52 unit of vinylbenzyl ether per molecule.

Example 25 - Thermal polymerization of 4,4'4''-tris[N-(3-(vinylbenzyloxyphenyl)-N-phenylamino]-triphenylamine

A sample of the tri-vinylbenzyl ether was dissolved in 1:1 chlorobenzene:toluene to give a 1 (weight/volume) percent solution. Excellent films on glass slides were obtained by spin-coating. A film was heated under nitrogen at 140°C for 4 hours. The I_{max} 333 nm intensity was measured. The film was then washed with xylene on the spin coater. The 333 nm peak intensity was 96 percent of that before xylene wash, indicating that the film was crosslinked. A similar film crosslinked onto a platinum electrode showed reversible oxidation potentials of 0.46 and 0.69 volt. Similar results were obtained from a resin solution containing 0.5 weight percent of t-butyl peroctoate.

Example 26 - Thermal polymerization of 4,4'4''-tris[N-(3-(2-acryloxyethyloxy)phenyl)-N-phenylamino]triphenylamine

A film of the resin is spin-coated from a toluene solution onto a glass slide and is then heated from 30°C to 175°C in 1 hour, and at 175°C for 3 hours under nitrogen. The cured film is rinsed with toluene on the spin-coater. The intensities of the UV absorption of the film before and after toluene rinse are identical, indicating that the film has been substantially crosslinked by the thermal treatment.

Example 27 - Photochemical polymerization of 4,4'-(2,2'-bis[4-(2-acryloxyethoxy)phenyl]-N,N'-diphenylamino)triphenylamine

A mixture consisting of the tri-acrylate resin, 1 phr of isopropylthioxanthone and 3 phr ethyl 4-dimethylaminobenzoate was dissolved in toluene to form a 2 percent solution. Films, cast on glass slides by spin-coating, were irradiated in a radiation curing device (Ultraviolet Crosslinker Model CL-1000, UVP, Inc.) with a 365 nm light source at 750 mJ/cm² for 30 minutes, at 500 mJ/cm² for 30 minutes, or at 500 mJ/cm² for 15 minutes. The absorption intensities of the films determined after rinsing with toluene were at least 85 percent of those before rinsing indicating that the films had been substantially crosslinked.

Example 28 - Electroluminescent Devices

A. Preparation of N,N'-diphenyl-N,N'-di-(4-chlorophenyl)-1,4-phenylenediamine

1-L, three-necked, round-bottomed flask, equipped with an overhead stirrer, a nitrogen inlet and a reflux condenser, was charged with N,N'-diphenyl-1,4-phenylene-diamine (13.0 g, 0.05 mol), 4-iodochlorobenzene (3.10 g, 0.13 mol), copper bronze powder (12.7 g, 0.20 mol), 18-crown-6 (2.6 g, 0.10 mol), powdered potassium carbonate (50.1 g, 0.36 mol) and 1,2-dichlorobenzene (120 mL). With a slow purge of nitrogen through the condenser, the reaction vessel was placed in an oil bath and the stirred reaction was heated at 200°C for 20 hours. The hot reaction mixture was filtered through a bed of filtering aid, which was washed with toluene (50 mL), and the filtrate was concentrated on a rotary evaporator under reduced pressure. The solvent residue was further removed with a Kugelrohr apparatus to afford a dark-brown viscous oil. Flash chromatography on a silica gel column (5 x 25 cm, 5 percent CH₂Cl₂ in hexane as eluent) afforded 9.6 g of grey-white solid. The crude product was further washed with toluene and acetone to provide 6.1 g (25 percent) of off-white powdered material.

B. Polymerization of N,N'-diphenyl-N,N'-di-(4-chlorophenyl)-1,4-phenylenediamine (PPPDA)

To a dry reactor equipped with a mechanical stirrer, nitrogen/vacuum inlet, and a rubber septum was added N,N'-diphenyl-N,N'-di-(4-chlorophenyl)-1,4-phenylenediamine (12.0 g, 25.0 mmol), triphenylphosphine (3.3 g, 12.6 mmol), zinc powder (4.9 g, 75 mmol), and NiCl₂-Bipy (0.22 g, 0.75 mmol). The reactor was evacuated to 3 mmHg then purged with nitrogen, this cycle was repeated five times. To the reactor was added via syringe 45 mL of N-cyclohexylpyrrolidinone and 27 mL of N-methylpyrrolidinone. The reactor was evacuated and purged with nitrogen an additional three times. The reaction was heated to 70°C in an oil bath with a stirring rate of 300 rpm. The grey heterogeneous mixture turned gradually to a red-brown liquid which became more and more viscous with time. The stirring was continued at 70°C for 10 hours and at 90°C for an additional 10 hours. At the end of the reaction, a dark green-brown viscous material was observed. The crude product was dissolved in hot

chlorobenzene (200 mL) and filtered through a short alumina column to remove the zinc dust. The filtrate was concentrated on a rotary evaporator to approximately 100 mL and the solution was once again passed through an alumina column eluted with chlorobenzene. The volume of the solution was reduced to approximately 100 mL and the polymer was precipitated with acetone (500 mL). The product was collected by filtration, washed with acetone and dried in a vacuum oven at 60°C overnight to give 9.53 g (93 percent) of light-yellow powders.

The product had the following properties: inherent viscosity, 0.16 dL/g in THF; $M_n = 6300$ daltons, $M_w = 14500$ daltons; $T_g = 222^\circ\text{C}$; reversible oxidation potentials, film (0.61, 0.96 v), solution (0.60, 1.03 v), and violet-blue fluorescence, solution and film.

C. Preparation of N,N'-diphenyl-N,N'-di-(3-chlorophenyl)-1,4-phenylenediamine

A mixture of palladium acetate (180 mg, 0.8 mmol), tri-*o*-tolylphosphine (536 mg, 1.7 mmol) and toluene (40 mL) was stirred at ambient temperature for 30 minutes until a homogeneous yellow solution was formed. To this solution were added N,N'-diphenyl-1,4-phenylenediamine (5.2 g, 20 mmol), 3-bromochlorobenzene (9.6 g, 50 mmol), sodium tert-butoxide (5.4 g, 56 mmol) and more toluene (120 mL). With a slow purge of nitrogen, the reaction vessel was placed into an oil bath and the stirred reaction was heated to reflux for 14 hours. The reaction mixture was cooled to ambient temperature, treated with hydrochloric acid (6 mL), and filtered through a bed of filtering aid. Removal of the solvent on a rotary evaporator under reduced pressure afforded a dark-brown viscous oil. Flash chromatography on a silica gel column (5 x 25 cm, 10 percent toluene in hexane as eluent) provided a light-yellow oil, which solidified on standing at ambient temperature. Recrystallization from methanol/acetone afforded 7.3 g (76 percent of product as white flecks) m.p 125°C to 127°C .

D. Polymerization of N,N'-diphenyl-N,N'-di-(3-chlorophenyl)-1,4-phenylenediamine (MPPDA)

To a dry reactor was charged N,N'-diphenyl-N,N'-di-(3-chlorophenyl)-1,4-phenylenediamine (1.2 g, 2.5 mmol), triphenylphosphine (327.5 mg, 1.25 mmol), zinc powder (490 mg, 7.5 mmol) and $\text{NiCl}_2\cdot\text{Bipy}$ (21.5 mg, 0.075 mmol). The reactor was evacuated to approximately 3 mm/Hg and was then filled with nitrogen. This cycle was repeated 5 times. To the reactor was added 3.5 mL of N-methylpyrrolidinone and the reactor was evacuated and filled with nitrogen 3 times. The reaction mixture was stirred and heated in an oil bath at 70°C for 20 hours. The polymer cake thus formed was dissolved in hot chlorobenzene (40 mL). The solution was filtered and concentrated to 10 mL. Acetone (100 mL) was added to the solution to precipitate the polymer as a white powder. Washing with acetone and drying in a vacuum oven at 60°C overnight gave 0.78 g (76 percent) of product which was identified by NMR as having the following properties: inherent viscosity of 0.12 dL/g in

CH_2C_{12} ; $T_g = 171^\circ\text{C}$; reversible oxidation potentials, solution 0.54, 0.96 v, and violet-blue fluorescence, solution and film.

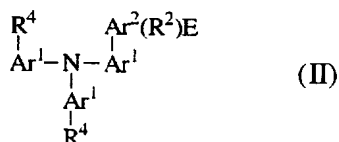
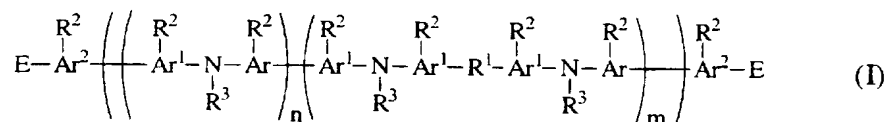
E. Preparation of Electroluminescent Devices

(a) A piece of ITO glass (20 ohm/square sheet resistance) was first coated with a
5 50 nm cured film of the branched amine of Example 26. Onto this film was deposited a 100
nm film of a linear polyamine PPPDA by spin-casting from a chlorobenzene solution. Onto
this was deposited a 120 nm of polyfluorene PFSE by spin-casting from methylcyclohexane
solution. Onto the PFSE film was deposited a 100 nm film of calcium by thermal evaporation
to complete device fabrication. When the device was biased with ITO as the anode and
10 calcium as the cathode, light emission from the PFSE layer was observed at 17 volt. At a
current density of 10 mA/cm^2 , the light output was 178 cd/m^2 .

(b) The above was repeated with the exception that the PPPDA film was replaced by
MPPDA film. Light emission was observed at 21 volt and 200 cd/m^2 light output was
observed at 10 mA/cm^2 current density.

CLAIMS:

1. A composition comprising at least one compound corresponding to Formula (I) or Formula (II):



wherein:

E is independently in each occurrence a hydroxy, glycidyl ether, acrylate ester, methacrylate ester, ethenyl, ethynyl, vinylbenzyloxy, maleimide, nadimide, trifluorovinyl ether, a cyclobutene bound to adjacent carbons on Ar², or a trialkylsiloxyl.

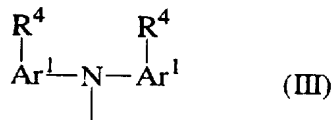
Ar¹ and Ar² are independently in each occurrence a di- or multivalent C₆₋₁₈ aryl moiety or a di- or multivalent C₄₋₁₇ aryl moiety containing one or more heteroatoms of nitrogen, oxygen or sulfur;

R¹ is independently in each occurrence a single bond; sulfur; oxygen; C₁₋₂₀ divalent hydrocarbyl; a divalent silyl or a polysilyl moiety bearing a C₁₋₁₀ hydrocarbyl; a C₁₋₂₀ divalent hydrocarbyl further containing one or more of oxygen, sulfur, an arylamine, a carbonyl, a carbonyloxy, an amide, sulfinyl, sulfonyl, an aryl phosphinyl, or an aryl phosphine oxide; or a C₁₋₂₀ hydrocarbyl-substituted siloxy or polysiloxyl;

R² is independently in each occurrence C₁₋₂₀ hydrocarbyl, C₁₋₂₀ hydrocarbyloxy, hydrocarbyl thioether, C₁₋₂₀ hydrocarbyl sulfonyl, C₁₋₂₀ hydrocarbyl sulfinyl, or two adjacent R² bonded to two aromatic rings which are bonded to the same nitrogen atom may form a direct bond between the two aromatic rings or be bonded to a divalent sulfur or oxygen;

R³ is independently in each occurrence a C₁₋₂₀ hydrocarbyl moiety or a moiety corresponding to the formula: -Ar¹(R²)-Ar²-E;

R⁴ is independently in each occurrence hydrogen, a C₁₋₂₀ hydrocarbyl moiety, -Ar²(R²)-E or a moiety corresponding to Formula (III):



with the proviso that each poly(tertiary di- or polyarylamine) contains two or more units which are -Ar²(R²)-E;

m is a number of from 0 to 50; and

n is a number of from 1 to 50.

2. A composition according to Claim 1 wherein:

Ar¹ and Ar² are independently in each occurrence derived from benzene, naphthalene, anthracene, phenanthracene, pyridine, thiophene, pyrrole, furan, diazine or oxazine;

5 R¹ is independently in each occurrence a single bond, sulfur, oxygen or a C₁₋₂₀ divalent hydrocarbyl;

R² is independently in each occurrence C₁₋₂₀ hydrocarbyl or two adjacent R² bonded to two aromatic rings which are bonded to the same nitrogen atom may form a direct bond between the two aromatic rings or be bound to a divalent sulfur or divalent oxygen; and

10 R³ is independently in each occurrence a C₁₋₂₀ alkyl, or C₆₋₁₈ aryl moiety or a moiety corresponding to the formula: -Ar¹(R²)-Ar²-E.

3. A composition according to Claim 2 wherein:

Ar¹ and Ar² are derived from benzene;

E is a hydroxy, glycidyl ether, acrylate ester, or methacrylate ester;

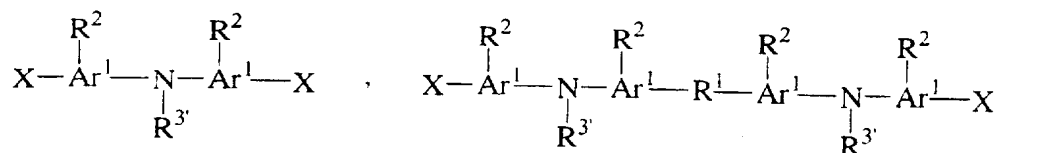
15 R¹ is independently in each occurrence a single bond, sulfur, oxygen or a divalent benzene moiety;

R² is independently in each occurrence C₁₋₁₀ alkyl or two adjacent R² bonded to two aromatic rings which are bonded to the same nitrogen atom may form a direct bond between the two aromatic rings or are bound to a divalent sulfur or oxygen;

20 R³ is independently in each occurrence a phenyl or a moiety corresponding to the formula: -Ar¹(R²)-Ar²-E; and

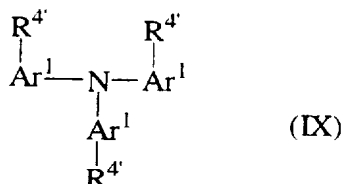
R⁴ is independently in each occurrence hydrogen, a methyl, -Ar²(R²)-E or a moiety corresponding to Formula (III).

4. A process for the preparation of a composition according to Claim 1 which
25 comprises contacting one or more tertiary di- or polyarylamines corresponding to one or more of Formulas (VII), (VIII) and (IX);



(VII)

(VIII)



with a haloaromatic compound having a reactive group capable of crosslinking or chain extension or a trialkylsiloxy moiety corresponding to the formula: E-Ar²-X in the presence of a catalytic amount of a divalent nickel salt, at least a stoichiometric amount of zinc powder, a trihydrocarbylphosphine and an amount of a compound capable of accelerating the reaction in a polar solvent and an optional co-solvent comprising an aromatic hydrocarbon or ether under conditions such that one or more compounds according to Formula (I) or Formula (II) is prepared,

wherein:

E is independently in each occurrence a reactive group capable of undergoing chain extension or crosslinking or a trialkylsiloxy;

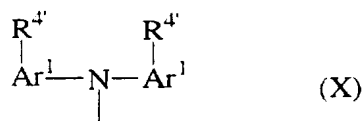
Ar¹ and Ar² are independently in each occurrence a di- or multivalent C₆₋₁₈ aryl moiety or a di- or multivalent C₄₋₁₇ aryl moiety containing one or more heteroatoms of nitrogen, oxygen or sulfur;

R¹ is independently in each occurrence a single bond; sulfur; oxygen; C₁₋₂₀ divalent hydrocarbyl; a divalent silyl or polysilyl moiety bearing C₁₋₁₀ hydrocarbyl; a C₂₋₂₀ divalent hydrocarbyl further containing one or more of oxygen, sulfur, an arylamine, a carbonyl, a carbonyloxy, an amide, sulfinyl, sulfonyl, an aryl phosphinyl, or an aryl

R² is independently in each occurrence C₁₋₂₀ hydrocarbyl, C₁₋₂₀ hydrocarbyloxy, C₁₋₂₀ hydrocarbyl thioether, C₁₋₂₀ hydrocarbyl sulfonyl, C₁₋₂₀ hydrocarbyl sulfinyl or two adjacent R² bonded to two aromatic rings which are bonded to the same nitrogen atom may form a direct bond between the two aromatic rings or be bonded to a divalent sulfur or divalent oxygen;

R³ is independently in each occurrence a C₁₋₂₀ hydrocarbyl moiety or -Ar¹(R²)X;

R⁴ is independently in each occurrence hydrogen, a C₁₋₂₀ hydrocarbyl moiety, X or a moiety corresponding to Formula (X):



with the proviso that two units per molecule are X; and

X is chlorine or bromine.

5. The process of Claim 4 wherein:

5 E is independently in each occurrence a hydroxy, a glycidyl ether, acrylate ester, methacrylate ester, ethenyl, ethynyl, maleimide, vinylbenzyloxy, nadimide, trifluorovinyl ether moiety or a cyclobutene bound to adjacent carbon atoms on Ar²;

Ar¹ and Ar² are independently in each occurrence derived from benzene, naphthalene, anthracene, phenanthracene, pyridine, thiophene, pyrrole, furan, diazine or oxazine;

10 R¹ is independently in each occurrence a single bond, sulfur, oxygen or a C₁₋₂₀ divalent hydrocarbyl;

R² is independently in each occurrence C₁₋₂₀ hydrocarbyl or two adjacent R² bonded to two aromatic rings which are bonded to the same nitrogen atom may form a direct bond between the two aromatic rings or be bound to a divalent sulfur or oxygen;

15 R³ is independently in each occurrence a C₁₋₂₀ alkyl, C₆₋₁₈ aryl moiety or a moiety corresponding to the formula: -Ar¹(R²)X; and

R⁴ is independently in each occurrence hydrogen, a C₁₋₁₀ alkyl moiety, X or a moiety corresponding to Formula (X).

6. A process according to Claim 5 wherein:

20 Ar¹ and Ar² are derived from benzene;

E is a hydroxy, glycidyl ether, acrylate ester, or methacrylate ester;

R¹ is independently in each occurrence a single bond, sulfur, oxygen or a divalent benzene moiety;

25 R² is independently in each occurrence C₁₋₁₀ alkyl or two adjacent R² bonded to two aromatic rings which are bonded to the same nitrogen atom may form a direct bond between the two aromatic rings or are bound to a divalent sulfur or oxygen;

R³ is independently in each occurrence a phenyl or a moiety corresponding to the formula: -Ar¹(R²)-X; and

30 R⁴ is independently in each occurrence hydrogen, a methyl, X or a moiety corresponding to Formula (X).

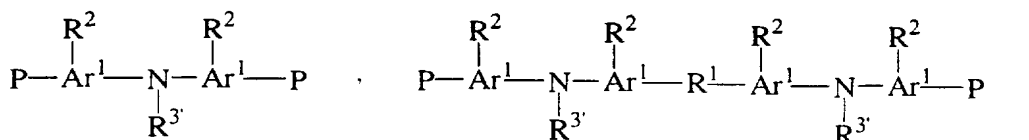
7. The process of Claim 4 wherein the mole ratio of tertiary di- or polyarylamines to haloaromatic compound having a crosslinking or chain extension moiety or trialkylsiloxy is from 0.5 to 50, the divalent nickel salt is present in an amount of from 0.01 to 20 mole

percent based on the amount of haloaromatic compound and tertiary di- or polyarylamine, the zinc powder is present in an amount of 100 mole percent to 300 mole percent based on the haloaromatic compound and tertiary di- or polyarylamine, the triarylphosphine is present in an amount of from 10 to 50 mole percent based on the haloaromatic compound and tertiary di- or polyarylamine and the amount of compound capable of accelerating the reaction is present from 100 to 150 mole percent based on the divalent salt.

8. A film comprising the composition of Claim 1.

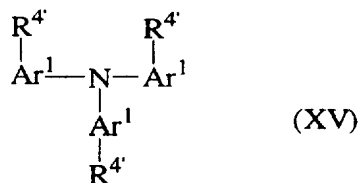
9. A polymeric light-emitting diode comprising a film according to Claim 8.

10. A process for the preparation of a composition according to Claim 1 which comprises contacting one or more tertiary di- or polyarylamines corresponding to Formulas (XIII), (XIV) and (XV):



(XIII)

(XIV)



with an aromatic compound having a reactive group capable of crosslinking or chain extension or a trialkylsiloxy moiety, corresponding to the formula: E-Ar²-Q in the presence of a catalytic amount of a zero valent palladium catalyst in the presence of heat or ultraviolet radiation under conditions such that one or more compounds according to one of Formula (I) or Formula (II) is prepared,

wherein:

E is independently in each occurrence a reactive group capable of undergoing chain extension or crosslinking or a trialkylsiloxy;

Ar¹ and Ar² are independently in each occurrence a di- or multivalent C₆₋₁₈ aryl moiety or a di- or multivalent C₄₋₁₇ aryl moiety containing one or more heteroatoms of nitrogen, oxygen or sulfur;

P is a boronic acid, chloro or bromo moiety,

with the proviso that one of P or Q must be a boronic acid moiety and the other

R¹ is independently in each occurrence a single bond; sulfur; oxygen; C₁₋₂₀ divalent hydrocarbyl; a divalent silyl or polysilyl moiety bearing C₁₋₁₀ hydrocarbyl; a C₁₋₂₀ divalent

hydrocarbyl further containing one or more of oxygen, sulfur, an arylamine, a carbonyl, a carbonyloxy, an amide, sulfinyl, sulfonyl, an aryl phosphinyl, an aryl phosphine oxide; or a C₁₋₂₀ hydrocarbyl-substituted siloxy or polysiloxy;

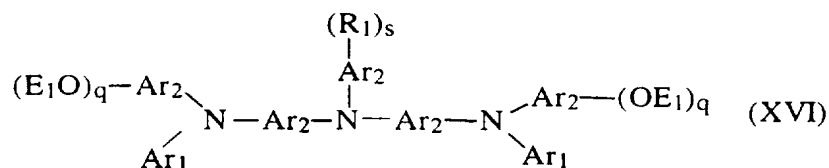
R² is independently in each occurrence C₁₋₂₀ hydrocarbyl, C₁₋₂₀ hydrocarbyloxy, C₁₋₂₀ hydrocarbyl thioether, C₁₋₂₀ hydrocarbyl sulfonyl, C₁₋₂₀ hydrocarbyl sulfinyl or two adjacent R² bonded to two aromatic rings which are bonded to the same nitrogen atom may form a direct bond between the two aromatic rings or are bonded to a divalent sulfur or oxygen;

R³ is independently in each occurrence a C₁₋₂₀ hydrocarbyl moiety -Ar¹(R²)X;

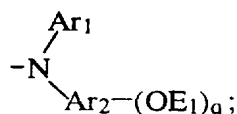
R⁴ is independently in each occurrence hydrogen, a C₁₋₂₀ hydrocarbyl moiety, X or a moiety corresponding to Formula (X); and

X is chlorine or bromine.

11. A compound of the formula:



wherein R₁ is independently in each occurrence hydrogen, or



Ar₁ independently in each occurrence is a C₆₋₂₀ aromatic group or C₃₋₂₀ heterocyclic group optionally substituted with up to 5 C₁₋₁₀ alkyl, alkoxy, thioalkoxy, aryloxy, or tertiary amine groups; Ar₂ is independently in each occurrence a C₆₋₂₀ aromatic group, optionally substituted with up to 4 C₁₋₁₀ alkyl, alkoxy, or thioalkoxy groups, E₁ is independently in each occurrence a C₁₋₂₀ hydrocarbyl radical, or a group capable of chemically reacting in a chain-reaction or step-reaction polymerization process at a temperature of less than 300°C at 1 atmosphere, with the identical group or other reactive groups attached to a separate monomer or polymer species, forming a covalent bond therebetween; and wherein the nitrogen atoms attached to the Ar₂ groups are located in positions which permit them to be in conjugation with any other nitrogen atom attached to the same Ar₂ group; q is an integer of from 1 to 4; and s is an integer from 1 to 4.

12. The compound of Claim 11 wherein Ar₁ is phenyl, biphenyl, or naphthyl.

13. The compound of Claim 11 wherein Ar₂ is phenylene, naphthylene, or fluorene.

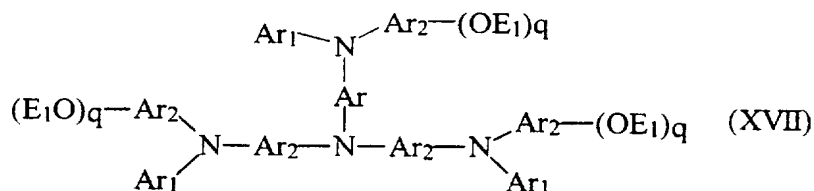
14. The compound of Claim 11 wherein E₁ is OH, methyl, benzyl, vinylbenzyl, methacryloyl or acryloyl.

15. The compound of Claim 11 wherein Ar_1 is phenyl, Ar_2 is phenylene, q is 1, and E_1 is hydrogen, methyl, or benzyl.

16. The compound of Claim 11 wherein Ar_1 is phenyl, Ar_2 is phenylene, q is 1, and E_1 is vinylbenzyl, methacryloyl or acryloyl.

5 17. The compound of Claim 11 wherein Ar_1 is phenyl, Ar_2 is phenylene, q is 1, and E_1 is: $-CH_2CH_2-O_2CCH=CH_2$.

18. A compound of the formula:



wherein:

10 Ar_1 independently in each occurrence is a C_{6-20} aromatic group or C_{3-20} heterocyclic group optionally substituted with up to 5 C_{1-10} alkyl, alkoxy, thioalkoxy, aryloxy, or tertiary amine groups;

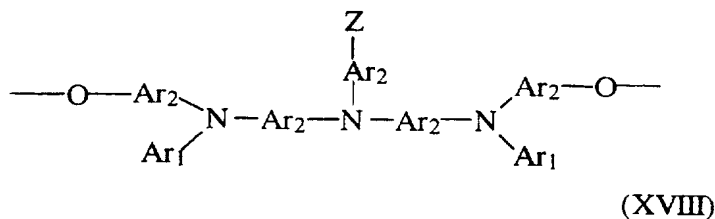
Ar_2 is independently in each occurrence a C_{6-20} aromatic group, optionally substituted with up to 4 C_{1-10} alkyl, alkoxy, or thioalkoxy groups;

15 E_1 is independently in each occurrence a C_{1-20} hydrocarbyl radical, or a group capable of chemically reacting in a chain-reaction or step-reaction polymerization process at a temperature of less than 300°C at 1 atmosphere, with the identical group or other reactive groups attached to a separate monomer or polymer species, forming a covalent bond therebetween; and wherein the nitrogen atoms attached to the Ar_2 groups are located in
20 positions which permit them to be in conjugation with any other nitrogen atom attached to the same Ar_2 group; and

q is an integer of from 1 to 4.

19. A polymer comprised of at least ten percent by weight of units derived from a reactive species of the compound of Claim 11.

25 20. A polymer having at least two units of the formula:



wherein:

Ar_1 independently in each occurrence is a C_{6-20} aromatic group or C_{3-20} heterocyclic group optionally substituted with up to 5 C_{1-10} alkyl, alkoxy, thioalkoxy, aryloxy, or tertiary amine groups;

Ar_2 is independently in each occurrence a C_{6-20} aromatic group, optionally substituted with up to 4 C_{1-10} alkyl, alkoxy, or thioalkoxy groups; and

Z is hydrogen, a C_{1-10} hydrocarbyl, alkoxy, thioalkoxy, aryloxy or a group of the formula: $-N(Ar_1)Ar_2-O-$.

21. The polymer of Claim 20 wherein Ar_1 is phenyl, biphenyl, or naphthyl.

22. The polymer of Claim 20 wherein Ar_2 is phenylene, naphthylene, or fluorene.

23. An electroluminescent device comprising a plurality of hole-transporting polymer films, at least one of which is the polymer of Claim 19, and a light-emitting polymer film, arranged between an anode material and a cathode material such that under an applied voltage holes are injected from the anode material into the hole-transporting polymer films and electrons are injected from the cathode material into the light-emitting polymer films when the device is forward biased resulting in light emission from the light-emitting layer and wherein the layers of hole-transporting polymers are arranged so that the layer closest to the anode has the lower oxidation potential, with the adjacent layers having progressively higher oxidation potentials.

24. An electroluminescent device comprising a plurality of hole-transporting polymer films, at least one of which is the polymer of Claim 20, and a light-emitting polymer film, arranged between an anode material and a cathode material such that under an applied voltage holes are injected from the anode material into the hole-transporting polymer films and electrons are injected from the cathode material into the light-emitting polymer films when the device is forward biased resulting in light emission from the light-emitting layer and wherein the layers of hole-transporting polymers are arranged so that the layer closest to the anode has the lower oxidation potential, with the adjacent layers having progressively higher oxidation potentials.